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MODERN DRY PLATES; OR EMULSION PHOTOGRAPHY

DR. J. M. EDER.

MODERN DRY PLATES;

OR,

EMULSION PHOTOGRAPHY.

BY

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THE AMERICAN EDITION,

EDITED BY

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PREFACE.

OUR task has been a light and pleasant one. To Mr. Horace Wilmer is due the credit of translating this little volume, and our own work has been confined to comparing authorities, and, in conjunction with the author, completing the manual so as to bring down its contents to the present day. In this respect the present publication may be regarded as a new edition of Dr. Eder's work in German.

There is no need to present Dr. Eder to an English-speaking public. His name as an ardent chemist and indefatigable experimentalist is too well known in the photographic world to need any words of introduction; and we feel sure that all who peruse these pages will not be ungrateful for the opportunity afforded them. It is not merely Dr. Eder's formulæ for the preparation of photographic emulsions, nor his advice relative to the mixing of developers, excellent as they are, that will be found most useful; but rather the clear and succinct manner in which he places before hardworking photographers, and *dilettanti* disciples of the camera alike, the whole theoretical and practical history of photographic emulsions. Dr. Eder's research on gelatine alone—the method of testing its purity, its setting qualities, and its general adaptability for plate working, as also the best plans for heightening or lowering its setting and melting points, of preserving it from decomposition, and adding to its firmness or elasticity—this research, in itself, must have entailed many months of laboratory work, and is a trite example of the thoroughness with which he has completed his task. The alternatives of boiling and adding ammonia are discussed at considerable length, and so are the means at the photographer's disposal to increase or decrease sensitiveness. Failures and remedies are not forgotten; and last, but not least, Dr. Eder furnishes simple methods of analysis, with a knowledge of which even those possessing but very moderate chemical attainments should be able to undertake an examination of any emulsions they may purchase or prepare.

H. BADEN PRITCHARD.

July, 1881.

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CHAPTER I.

THE HISTORY OF EMULSION PHOTOGRAPHY.

COLLODION EMULSION.

THE idea of preparing an emulsion with a sensitive salt of silver, so as to supersede the use of the sensitizing bath, has been discussed for more than twenty-five years. In 1853, Gaudin, writing in *La Lumière*, stated that the whole future of photography seemed to require a sensitive collodion which could be preserved in a flask and poured upon glass or paper, and, by the use of which, either at once, or after the lapse of time, positive or negative pictures could be obtained. The possibility of an iodide or chloride of silver emulsion, such as he described in 1861, and to which he gave the name of "Photogen," was clearly even then before his mind.[1] This collodion emulsion—the first in the strict sense of the word—proved so sensitive, that Gaudin found it possible to employ the same on wet plates, and believed it might also be used with advantage on paper in the camera. He moreover suggested the employment of collodio-chloride of silver, prepared with ammonium chloride, and nitrate

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[1] *Photographic News*, 1861, v., 408 ; *Photographic Notes*, 1861, vi., 156.

of silver, instead of the ordinary sensitized positive paper. It was not, however, till September, 1864, that collodion emulsion, with bromide of silver—since become so familiar—was published as a practical and independent process. The discovery was made by Sayce, and was afterwards accurately described by him and Bolton, in the PHOTOGRAPHIC NEWS.[1] In some further particulars published in 1865, differing, however, in no essential degree from those already given, he describes almost all the modifications of emulsions since investigated, namely:

1. Trituration of a bromized collodion with solid nitrate of silver.
2. Introduction of an alcoholic solution of nitrate of silver into a bromized collodion.
3. Precipitation of bromide of silver from aqueous solutions of potassic bromide and nitrate of silver, followed by washing first in water, then in alcohol, and, after entire removal of water, emulsification of the precipitate in collodion.

As I have pointed out, the latter method was suggested by Sayce as early as 1865, although Carey Lea described it again in 1874, and de Lafollye communicated it as a novelty in 1879.

Sayce and Bolton had already published in 1864 the fact that collodion emulsion prepared with excess of soluble bromide proved very insensitive unless some body was present to act as an accelerator. They therefore treated the plates with tannin, gallic acid, grape sugar, &c. The advantage of washing the emulsion was already known.

In 1865 Bolton communicated an accurate formula for the preparation of an emulsion containing an excess of nitrate of silver.[2]

Bromide of silver emulsions containing an excess of nitrate of silver were at first always treated with a preservative. Sutton brought forward, in 1871, for the first time, a collodio-bromide

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[1] *Photographic News*, 1865, ix., 805.

[2] *Photo. Arch.*, 1866, vii., 53.

process without a preservative, which consisted simply of an unwashed emulsion containing excess of nitrate of silver.

The idea that, under all circumstances, a preservative was of value, was strongly opposed by Stuart Wortley, who contended that an organic substance in the presence of nitrate of silver has no influence in increasing the sensitiveness.[1] This view was also expressed by Vogel and Warnerke, and is at the present time generally accepted.

In 1875 Newton discovered that a sensitive collodion emulsion could be prepared by allowing the bromide of silver to ripen in the presence of an excess of nitrate of silver, such excess being afterwards removed by the addition of either cobaltic or calcic chloride. Chardòn made use of this principle in his process, for which a prize was given by the French Photographic Society.[2]

Bardy was the first to point out the possibility of successfully employing other solvents besides alcoholic ether in the preparation of a collodion emulsion—for instance, alcohol, acetic acid, acetone, &c.[3]

The pioneers of the bromide emulsion processes had turned their attention from the first to the employment of alkaline pyrogallic development, the principles of which had been communicated for the first time by Russell in 1862.[4]

Collodio-chloride of silver for printing purposes (without development)[5] was described in 1865 by Mr. George Wharton Simpson, a former editor of the PHOTOGRAPHIC NEWS, and will be found described in the pages of that journal for 1865, ix., 121.

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[1] *Br. Journ.*, 1876, xxiii. 65.

[2] "Photographie Emulsion Seche au Bromure d'Argent," Paris, 1877.

[3] *Bull. Soc. Franç.* 1879, 210.

[4] *Br. Journ.*, 15 Nov., 1862.

[5] *Photo. Arch.*, 1865-6, 184; *Photo. Corr.*, 1865, ii., 247; *Photo. News*, 1865, ix., 121.

The first intimation that chloride of silver was, like bromide of silver, susceptible of alkaline development, was made by H. Russel in 1867.

[illegible] ?

GELATINE EMULSION.

In his first paper on the subject of collodion emulsions, 20th August, 1853, Gaudin alluded to analogous experiments which he had made with albumen and gelatine.

On the 8th September, 1871, Maddox published his first notice of the preparation of a gelatine emulsion, and at the same time handed Mr. Traill Taylor several landscape and other negatives produced by the new process.[1]

In a communication dated 14th November, 1873, King directed that the soluble salts should be removed by washing, and on the same date, Johnson recommended the employment of an excess of soluble bromide.[2] The latter point was to be afterwards recognized as of the highest importance, and now-a-days, no gelatine emulsion is prepared which does not contain a small excess of soluble bromide.

The first gelatine emulsion commercially produced was that of Burgess, advertised for sale in 1873. Although the formula was not given, we may credit him still with having been the first to produce a true gelatine emulsion on a commercial scale. The earliest washed emulsion in the form of pellicle was brought into the market by Kennett, in 1874, and a description of his process was published in April of the same year.[3]

Wratten and Wainwright suggested, in the YEAR-BOOK OF PHOTOGRAPHY for 1878, a new method of washing the emulsion, by squeezing the jelly through canvas.[4]

A communication made by Bennett, on the 29th March, 1878,

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[1] *Photo. Cor.*, 1874, xi, 124.

[2] *Ibid*, p. 126.

[3] *Br. Journ.*, 1874, xxi., 291.

[4] *Year-Book of Photography*, 1878, 108.

to the effect that prolonged digestion at a temperature of 32° C. conduced to great sensitiveness, marks an important era in the history of very sensitive gelatine emulsions.[1]

It is important to record the application of Dr. Van Monckhoven to the study of the new process in August, 1879. He pointed out at once that the increase in the sensitiveness of an emulsion caused by prolonged digestion was accompanied by a molecular change. After recalling the various communications of Stas, in 1874, in regard to the various modifications of bromide of silver, he made the important statement that the conversion of the latter into the sensitive green modification could be materially hastened by the use of ammonia.

In June, 1879, Capt. Abney suggested a method which had long ago been attempted in the case of collodion emulsion, that of precipitating bromide of silver from aqueous solutions, and emulsifying the washed precipitate in gelatine. This process, however, has not been extensively adopted up to the present time.[2]

It is interesting to record the fact that as far back as 1866 Palmer and Smith described in the *Photographic News* a process for printing with gelatino-chloride of silver.[3]

According to the instructions subsequently given by Palmer, paper coated with this emulsion may be used for printing, or after fuming with ammonia it has also been employed for printing on opal glass, as well as for producing developed enlargements on canvas in the solar camera.

Further details connected with the history of emulsion processes will be found here and there in the text, but an exhaustive treatise on this subject would be beyond the scope of this work.

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[1] *Photo. Corr.*, 1878 and 1879.

[2] *Journ. Photo. Soc. of Gt. Brit.*, iii., 59; and *Photo. Corr.*, 1879, xvi., 104, 248.

[3] *Photographic News*, 1865, ix., 613; 1866, x., 24, 36; *Photo. Mitth.*, 1866, ii., 141.

CHAPTER II.

BEHAVIOUR OF THE HALOID SALTS OF SILVER IN EMULSIONS.

In a treatise on the "Photo-Chemistry of Bromide of Silver" which I brought before the Royal Academy of Vienna, on the 4th March and 8th April of last year, will be found some extracts from a larger work which I consider would be of interest to students of chemistry and physics. Since the publication of these papers in the Proceedings of the Society, I have made numerous additions in the way of observations relating to the practice of photography, and in publishing the result of them in this work, I venture to hope that they will lead to useful results. The majority of experiments were made with the assistance of Capt. Toth, and refer generally to the latent action of light as manifested by chemical development; and more particularly to bromide of silver emulsions for the production of developed negatives.

The behaviour of the haloid salts of silver in the presence of light, and their chemical development,[1] has never been accurately determined, in spite of the interest displayed in the subject on the introduction of the Daguerreotype, and the investigations, particularly those of Dr. Vogel, of more recent times.

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[1] Under the term "chemical development," we mean that bromide of silver, altered by the action of light, is itself reduced to the metallic state by the action of an alkaline solution of pyrogallic acid, or of ferrous oxalate. In the case of physical development, there is no such reduction of the film, but the silver is precipitated by the action of the ferrous sulphate developers, or by vapour of mercury in the case of Daguerreotype, and deposited in nascent state on the film to form the picture.

Acting on this idea, I have chosen the subject as a field for further investigation, to embrace generally the photo-chemical principles of modern photography. In my experiments I employed emulsions, as I found that in this form the state of division of the haloid salts is extremely fine, and the film is in its most homogeneous condition[1]. On the other hand, plates sensitized in the bath display a variable composition on the upper side of the film, and this variation could be detected simply by pouring on the developer. The behaviour of the haloid salts of silver will be found to differ according as they are contained in an indifferent medium, or in one easily oxidized. It was evidently necessary, therefore, not only to study the influence of these two classes of substances, but also to investigate the action of other bodies, such as free halogen, oxidizing substances, free acids, the various forms of haloid salts, alkalis, ammonia in particular, bodies absorbing halogens, and bodies which act on account of their optical properties. Equally important were the effects of temperature, of solution, the action of coloured rays of light, quality of chemical developer, the function of electricity during development, the decomposition produced in bromide of silver by other agents, and, finally, the behaviour of bromide of silver towards the other haloid salts of silver as regards sensitiveness.

I.—BEHAVIOUR OF BROMIDE OF SILVER COMBINED WITH AN INDIFFERENT SUBSTANCE (COLLODION).

A collodion pyroxylin may be classed as an indifferent substance, especially after it has become purified by washing with alcohol and repeated precipitation in water, and re-dissolution in alcoholic ether. This body is extremely stable, and offers no

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[1] To 100 parts of a solvent—such as water or ether and alcohol—I add usually from 3 to 6 parts of silver nitrate, and from 3 to 9 parts of the combining medium, either gelatine or collodion pyroxyline. The secondary product so formed in the presence of a slight excess of the solvent can be removed by washing.

inducement to bromide of silver to decompose under the action of light.[1] If an alcoholic solution of silver nitrate be introduced into a bromised collodion, and the whole well shaken, the emulsion is readily formed, and the flakey bromide so produced passes in a short time into the fine modification;[2] but in my experience, a change occurred in the transparency or so-called "ripening" of the emulsion during the two or three days necessary to complete its conversion.

The formation of the fine granular modification can never be observed in an alcoholic ether solution, unless ammonia be added.[3]

Excess of Silver.

Bromide of silver prepared with an excess of silver nitrate appears in thin films, white by reflected light, and transmits more of the violet than the red rays.

It proved, even after careful washing, until no further trace of silver was apparent, about twice or three time as sensitive[4] as

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[1] Collodion does not act as a sensitizer, in the case of iodide of silver, with physical development.

[2] I shall adhere rigidly to the modifications of bromide of silver described by Stas in his valuable paper ("Annales de Chemie et Phys.," vi., 8, 1874; *Photo. Mitth.*, xvi., 165.)

[3] This may possibly depend on the fact that alcoholic ether does not show in the slightest degree the capacity possessed by water of dissolving bromide of silver. Even when heated, not a trace of the bromide of silver dissolves in the collodion: nor does the modification formed partake of the granular description, but the bromide separates in clots. It is impossible to detect any change of colour or increase in grain, facts which are so apparent in the case of gelatine emulsion.

[4] The comparison of sensitiveness was made with a Steinheil aplanatic lens. A plaster cast containing strong contrasts of light and shade was employed as the object to be photographed, and the developers used were pyrogallic acid and ferrous oxalate. The standard of sensitiveness was based on the undisputed theory that the sensitiveness to light of any compound varies inversely with the time necessary to produce any given effects.

an emulsion prepared with excess of soluble bromide, and in addition was more readily acted on by the developer.

This exalted sensitiveness may be due chiefly to the presence of a trace of silver nitrate, so firmly suspended in the collodio-bromide as to be incapable of removal, even by boiling water. In the case of iodide or bromide of silver with physical development, silver nitrate plays the part of an accelerator, and further evidence of its action in increasing the sensitiveness will be afforded by the following facts. If silver nitrate to the extent of one per cent. be added to a washed bromide of silver emulsion, its sensitiveness is so much increased as only to require about one-half to one-third the exposure necessary in the case of a corresponding emulsion containing no such excess. Any further addition of silver nitrate, beyond two to three per cent., produces no corresponding increase of sensitiveness, and chemical fog makes its appearance during development, a fact which does not surprise me, as I have already proved that silver nitrate can be reduced instantly under the action of ferrous oxalate without any previous exposure to light.

The conversion of the flocculent bromide into a state of fine division takes place also more readily in the presence of a trace of silver nitrate than in the presence of a soluble bromide.

Excess of Soluble Bromide.

Bromide of silver prepared with excess of soluble bromide is yellow by reflected light, and, in the case of thin films, transmits red light. Even after careful washing it is, as I have stated above, less sensitive than when an excess of silver nitrate is employed. This fact appears to be owing rather to the absence of silver nitrate, than to the presence of potassium bromide, for in the case of bromide of silver prepared with excess of silver nitrate, the same falling off of sensitiveness appears to result, whether the free silver be removed either by the use of sodic chloride, or potassium bromide, followed by careful washing.

As an increase of sodic chloride from 0·1 to five per cent. failed to produce any corresponding decrease of sensitiveness, I concluded that the latter in itself had no practical effect.

The case of an excess of soluble bromide, such as cadmium or potassium, is different, and, under the influence of such bodies, the sensitiveness of bromide of silver will be found to fall off in rapidly increasing proportion. Bromide of silver containing from one and three-quarters to two per cent. of ammonium bromide in excess, will be found only half as sensitive as a washed bromide of silver. A larger excess affects the sensitiveness still more.

II.—BEHAVIOUR OF BROMIDE OF SILVER WHEN CONTAINED IN ORGANIC SUBSTANCES WHICH ARE EASILY OXIDIZED, SUCH AS GELATINE, GUM, ETC.

Gelatine and gums are admirably adapted for this purpose, as they are very favourable to the decomposition of silver salts in the presence of light, and, besides this, they are readily obtainable. Gelatino-bromide of silver prepared with *excess of silver nitrate* is only slightly more sensitive after washing than one prepared with excess of soluble bromide which has also been washed, although the former sometimes gives denser pictures. A considerable excess of silver nitrate causes a decomposition of the emulsion, without exposure to light. Plates coated with an emulsion of this description turned brown spontaneously without having seen light. Bromide of silver prepared with excess of silver nitrate is, even after careful washing, more liable to decompose under high temperatures and long digestion than the same prepared with excess of soluble bromide, and after this decomposition, which is invisible to the eye, has taken place, the resulting emulsion is less sensitive than the latter. When precipitated with excess of silver nitrate according to Abney's method, washed and emulsified in gelatine, it gives, after twenty-four hours' digestion, thinner negatives than after two days.

According to Dr. Szekely's experiment, the intensity went on increasing up to the sixth day, as well as the size of grain of the bromide of silver, just as in the modification previously described, in which an excess of soluble bromide was employed.

Judging by the perfect quality of Dr. Szekely's original plates, as regards vigour and detail in the shadows, I concluded that the photographic properties of bromide of silver precipitated with excess of silver nitrate, and then washed, were improved by protracted digestion under heat, and that this was accompanied by an increase in the size of the grain.

Besides, it is probable that the first stage of the ripening process, which is most apparent to the eye, is incapable of control by this method, since the commencement of digestion is accompanied by a separation of the bromide of silver into large flakes.

Bromide of silver precipitated from an excess of silver nitrate, and washed, must not be considered more sensitive than the same prepared with excess of soluble bromides by any of the methods given for compounding highly sensitive emulsions; in fact, it is less so. In addition to this, as I have previously pointed out, there is always a tendency towards the decomposition of the emulsion during long digestion or cooking for a short time, owing to the absence of the beneficial restraining action of the soluble bromide.

Excess of Soluble Bromide.

Gelatino-bromide of silver prepared with a small excess of soluble bromide at 35° C. is, after twenty-four hours' digestion, at least six times as sensitive as the same bromide combined with an excess of silver nitrate in an indifferent collodion, and twenty to forty times as sensitive as collodio-bromide prepared like the gelatine emulsion, with excess of soluble bromide. A large excess of a soluble bromide, such as potassium or ammonium, often lowers the sensitiveness from a half to one third. Such an excess must be avoided or removed by washing. Gelatine emulsions prepared with excess of soluble bromide require very careful washing. A neglect of this precaution results in an insensitive emulsion, which gives hard negatives.

That gelatine acts as a sensitizer is clearly proved by the fact that an insensitive modification of bromide of silver, emulsified in gelatine with an excess of soluble bromide, is not essentially less sensitive than the sensitive modification of the former, emulsified with nitrate of silver. We can only compensate for the absence of silver nitrate in the former case by introducing some other sensitizing body. The sensitizing action of gelatine in the case of collodio-bromide, prepared with excess of bromide, is proved by the increase of sensitiveness consequent on applying a coating of gelatine to these films. According to Vogel's theory, it is a sensitiser in the strict sense of the word, as well as isinglass and glue, which, by Knopps' analysis (1879), after digestion with bromine water for from two to four days at ordinary temperature, combine chemically with 20·5 to 22·9 per cent. of bromine, and bromised organic matters are thrown down in the form of a yellow powder.

Character of the various Modifications of Bromide of Silver.

The finely-divided form of bromide of silver, modifications of which will be found described below, is the kind most generally employed. The flocculent description prepared with excess of bromide, and suspended in gelatine, is extremely insensitive. I heated on one occasion bromide of silver of such a character in glycerine for more than half an hour, at a temperature as high as 100° C., and on the addition of gelatine, and development with ferrous oxalate, it proved still less sensitive than the worst form of finely-divided bromide emulsion.

If an aqueous gelatino-bromide of silver emulsion be digested at temperatures ranging between 30° C. and 50° C., the bromide of silver passes from its original fine powdery condition into the fine granular state, and the same change occurs that Stas has so accurately described, in the case of boiling bromide of silver with water. I watched this operation under a microscope, and found, in one special case, that after digestion continued for five days, the particles of bromide of silver had increased from ·0008 m.m. up to ·003.[1] Stas and Vogel consider that it is owing to this cause that the sensitiveness of an emulsion kept warm for a long time according to Bennett's method,[2] is so great; and, so far as my own observations are concerned, there is no doubt of it. Monckhoven[3] has also called attention to the change of colour which accompanies this conversion, the bromide of silver appearing green by reflected light; but the most distinctive feature is the grey-blue colour which the emulsion will be found to possess by transmitted light. The changes of colour in the emulsion by transmitted light are so characteristic, that I strongly recommend, in the preparation of every emulsion, the coating of a test-plate, as a means of watching these changes. The plate should be examined immediately after coating, or, at all events, before the emulsion is dry,[4] otherwise the colour is apt to change. Care

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[1] An alcoholic ether collodion emulsion will never give this appearance, even when heated, or when allowed to ripen for as long as two years.

[2] *Photographic News*, 1878. *Photographische Correspondenz*, 1878, xv., 212; 1879, xvi, 87.

[3] *Bulletin de l'Association Belge*, 1879. *Photographische Correspondenz*, 1879, xvi., 149.

[4] An unwashed emulsion, owing to the presence of by-products, is apt to change in colour by transmitted light when dry. The test should, therefore, be made before the salts crystallize out.

must also be taken not to expose the plate to light for more than a few minutes, otherwise it will be found that the colour changes rapidly, and experiments made by Toth and myself prove that an insensitive emulsion which transmits orange light will, after exposure, transmit blue light, and appear more green by reflected light, than the highly sensitive modification of that colour.

Gelatino-bromide of silver, digested during periods ranging from three to six days, becomes so extraordinarily sensitive, that combined with ferrous oxalate development, its sensibility to light is far in advance of any body known up to this date. I am convinced that dry bromide of silver plates prepared by any ordinary method, and chemically developed, are from five to ten times as sensitive as iodide of silver plates prepared with a concentrated silver bath, and physically developed, and later on I shall discuss a method of obtaining still greater sensitiveness. These remarks apply principally to bromide of silver prepared with excess of free bromide. That prepared with excess of silver is apt to decompose during digestion.

The change in the finely-divided granular bromide of silver mostly takes the form of a considerable increase in the size of grain when the digestion is protracted for a considerable time, say from eight to fourteen days. It forms into nodules of about ·02 to ·04 m.m. in diameter, which are quite apparent to the naked eye, and in this case we have an emulsion which fogs, without previous exposure to light, under the action of the developer. If there be no excess of alkaline bromide, any temperature above 60° C. favours the formation of the nodules, but an excess of the former retards the production to some extent. It is remarkable that the larger particles of the fine granular bromide of silver are reduced more easily under the action of the developer than the smaller particles of the fine powdery kind. For instance, the large grains of bromide of silver previously described are reduced by a normal developer, without any previous exposure to light.[1] The capacity of bromide of silver for chemical reduction, as well as for decomposition in presence of light, depends on an increase in the size of grain. The size of grain forming the metallic image of the developed and fixed negative will correspond entirely with that of the unreduced bromide of silver.

For experimenting with gum-arabic emulsions, I took advantage of the influence which increase of temperature has on gelatine emulsions. The former were prepared sometimes cold, and at other times digested for six days, at temperatures of 30° or 40° C., after which gelatine was added, and the emulsion washed. Those digested with heat were more sensitive, and transmitted less red light, than those prepared cold. There was no marked increase of sensitiveness after many weeks' digestion at 12° to 15° C., nor had the conversion into the sensitive modification taken place after standing at ordinary temperatures for three weeks. I cannot recommend Mawdsley's and Bruyère's[2] suggestion of emulsifying bromide of silver in gum, for the following reasons:

1. If emulsified cold, the sensitiveness of the emulsion is very inferior.

2. Although when emulsified with heat, or with addition of ammonia, it readily acquires sensitiveness, still the plates show such an obstinate tendency to frilling and expansion of the film, that this proceeding appears to be impracticable. On the whole, we may conclude that if heat is to be employed, it is advisable to adhere to the ordinary gelatine process.

The sensitiveness of a washed gelatine emulsion appears to improve by keeping, and indeed, according to Abney, after three days such increase becomes considerable.

If a gum or gelatine emulsion containing potassium bromide and silver nitrate in the proportion of four to five be digested at

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[1] These observations were made in the course of careful microscopic measurements and comparison of various plates, both before and after development.

[2] *Year-Book of Photography*, 1881, 145.

temperatures varying from 32° C. to 48° C., the white bromide of silver passes very slowly into the green modification. At the end of six days, however, the conversion is far advanced; the films transmit more violet light, and are very sensitive. If the digestion be carried further, fog supervenes. An hour's digestion at 60° C. produces a highly sensitive emulsion, and if prolonged to four hours, the same degree of sensitiveness is attained which is produced by more than four days' emulsification at a temperature of only 40° C.

A further cooking of seven and even thirteen hours at 60° C. showed no change of note; the plates were exceedingly sensitive, and developed free of fog.[1] An emulsion cooked for a short time (say from two to five hours at 60° C.) was more rapid than one digested for an equally short time at from 30° to 46° C., but not so good under all circumstances as one which has stewed for five to seven days at the latter temperatures. However, I conclude that the object in view is attained more rapidly by a short cooking at a high temperature, and the operation, owing to its shortness of duration, can be more carefully watched than in the case of prolonged digestion.

The most rapid method of obtaining great sensitiveness is by raising the temperature to boiling point. We can in this way obtain by half an hour's boiling the same sensitiveness as is yielded by five to six days' warming at 35° to 40° C. The boiling should not be carried beyond half an hour. Indeed bromide of silver prepared with a large excess of potassium bromide, and boiled for an hour and a half, decomposed in the course of our experiments to such an extent, that in development the picture became buried in a deep fog.[1] A good deal of advantage is to be derived by heat-

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[1] The priority of discovering that a gelatino-bromide of silver emulsion cooked at a high temperature reaches its sensitive condition more rapidly than when temperatures of 37° or 40° C. are employed, belongs to two Englishmen. Wortley pointed out that a gelatine emulsion cooked for a few hours at 67° was quite as sensitive as one digested for several days at a

ing the solutions of potassium bromide and gelatine up to 60° C. or 70° C., before the introduction of the silver. The sensitive state is more rapidly attained by this method than by precipitating bromide of silver from cold solutions, and heating afterwards (see page 33, on the possibility of spontaneous decomposition). The conversion of bromide of silver into the highly sensitive state is retarded by a large excess of soluble bromide. The proportion of the latter to silver nitrate in an emulsion should not exceed four to five as determined by Capt. Toth and myself, or seven to four as recommended by Bennett, for if the excess of alkaline bromide be very large, fog ensues (see page 33).

In these processes, the power of water to dissolve bromide of silver probably plays some part. The formation of the granular bromide certainly proceeds more rapidly in a solvent, and it is on this granularity, as we know, that the sensitiveness of gelatino-bromide of silver depends.[1] Gelatine restrains the precipitation of chloride of silver, and partially that of bromide of silver, while if digestion with heat be employed, the silver compound becomes partially redissolved. If a larger proportion of bromide of silver exists in the water, the consequent increase of sensitiveness may possibly be due to the presence of a small portion of bromide of silver in solution.

III.—EFFECT OF FOREIGN BODIES ON BROMIDE OF SILVER, AND ON THE FORMATION OF THE LATENT IMAGE.

Influence of Free Halogens.

Free halogens, chlorine, bromine, or iodine, whether in solution or in form of gas, destroy the sensitiveness of every form of

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lower temperature (*Phot. Mitth.*, 1876, xiii., 13). It is not so well known, however, that Mansfield, at the meeting of the Irish Photographic Society, in August, 1879, stated that boiling an emulsion for ten minutes produced as good a result as digesting for some days in lukewarm water.

[1] Pointed out by Hardwich in 1860 (Journ. Photo. Soc., vi., 116).

bromide of silver, when allowed to act on a plate before exposure to light, or if after exposure, they destroy the previous action of light, and there is no means of reproducing the latent image. These remarks apply to collodion or gelatine plates with either form of development, as well as to Daguerreotypes. It has been customary, according to Abney, to employ tinctures of bromine or iodine to restore the sensitiveness of an emulsion which has been spoiled by admission of foreign light. It is necessary, however, under any circumstances, to remove, either by use of ammonia or by a method which will be given later, all excess of bromine or iodine; for a small trace of either of these bodies, or of the corresponding hydrogen acids, will degrade the sensitiveness of the bromide of silver.

Effect of Ozone.

Reynolds was the first to point out the effect of ozone in removing the latent image from an iodide of silver film.[1] According to Abney, it operates in a similar manner on bromide of silver.[2] Oxygen, too, tends to produce the same effect.

Effect of Nitrous and Nitric Acids.

Abney has already described the injurious effects which nitric acid has on bromide of silver, and, as far as my experience goes, it destroys the latent image in a very short time. The presence of nitric acid, even in small quantities, destroys the sensitiveness of bromide of silver to light; and, in one case, I found that the addition of 1 per cent. of nitric acid reduced the sensitiveness of an emulsion by one-fifth. In a concentrated form it is quite as injurious as chlorine water. The effect is least apparent in the case of a collodion emulsion prepared with excess of silver; indeed, in this case, the presence of a small quantity of nitric acid is useful

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[1] *Les Mondes, par Moigno*, xvi., 477.

[2] *Bull. de l'Association Belge*, 1878, iv., 258.

in restraining the inherent tendency to fog. When an emulsion is prepared with excess of silver bromide, a small quantity of nitric acid reduces the sensitiveness to a remarkable extent when the proportion of this soluble bromide is not considerably in excess of the nitric acid. Sherman has stated that it is possible to entirely desensitize bromide of silver plates by means of a mixture of nitric acid and ammonium bromide. Abney finds that while nitric acid destroys the latent image in the case of a bromide film, it has no such effect on an iodide film. This seems to point to the fact that the image on an iodide of silver plate is not formed by a deposition of metallic silver.

Oxidizing Bodies.

According to Abney, bichromate of potash, alkaline permanganates, and peroxide of hydrogen have on bromide, as well as on iodide films, the same effect as ozone, namely, that of destroying the latent image.[1] This fact may be made use of in order to restore the sensitiveness of a foggy emulsion.[2] Abney directs that such an emulsion should be squeezed through canvas into a ½ per cent. solution of bichromate of potash, allowed to remain in it for four or five hours, and then well washed. The treatment with bichromate, however, reduces sensitiveness, even with thorough washing (see ch. xi.). Fog can be entirely got rid of by this means, and the emulsion will give clear, brilliant negatives.

Sulphuretted hydrogen and coal gas have a destructive action on the latent image. If an excess of silver nitrate be present, it is reduced by the latter to the metallic state.

Free acids—hydrochloric, sulphuric, and hydrobromic—although not so injurious as oxidising bodies, destroy the latent image if they are allowed to operate on bromide of silver for a length of time. Organic acids, such as acetic or citric,

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[1] *Photo. Corr.*, 1878.

[2] *Photo. News*, 1880, xxiv., 328.

have a like tendency, to a small extent, in the case of bromide of silver prepared with excess of bromide; but if the silver be in excess, I have not found any decomposition result from the presence of these bodies. Bolton recommends the use of citric acid as a restrainer of fog in the case of collodion emulsion containing an excess of silver.[1] An acid reaction likewise retards chemical fog in the case of bromide of silver.

Effect of other Salts and Ammonia.

Perchloride of iron, perchloride of copper, and iodide of potassium entirely remove the latent image. Mono-bromides, such as bromide of potassium or ammonium, and mono-chlorides, such as sodium-chloride, have a retarding effect on development in various degrees.[2] Cyanide of potassium gives very clean negatives when present in a bromide emulsion; but it destroys the latent action of light if present in a slight excess. These facts, which are familiar to collodion emulsion workers, will be found equally applicable to gelatine emulsion. Cyanide of potassium in the case of a gelatine emulsion gives very thin negatives, and is apt to induce liquefaction. Uranium nitrate has no direct effect, although Stuart Wortley recommends it for gelatine, as well as for collodion emulsions.

Alkalies generally assist the action of light. The sensitiveness of an emulsion will be found to be doubled if carbonate of soda, carbonate of ammonia, or ammonia be added to it, or if plates be soaked in solutions of these bodies. The same effect occurs in the case of a gelatino-bromide emulsion digested at a temperature not exceeding 40° C., and is accompanied in my experience with an increase of size in the grain of the bromide of silver. A normal addition of ammonia gives a grain of moderate size, such as is apparent in the ordinary sensitive modifi-

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[1] *Br. Jour.*, 1878, xxv., 428.

[2] A boiling solution of bromide of ammonium totally destroys the image.

cation, and which does not interfere with the delicacy of the picture. The addition of more ammonia gives a coarse grain, which is visible in the resulting print. I obtained this effect, on one occasion, by digesting for six hours, at a temperature frequently exceeding 40° C., a gelatine emulsion to which 3 per cent. ammonia had been added. Gelatine digested for some time with 5 per cent. of ammonia loses its power of setting; and if stewing be prolonged for twelve to twenty-four hours, the bromide of silver is partially decomposed, and is rapidly reduced by ferrous oxalate without any exposure to light being necessary; and as this chemical decomposition follows in proportion to the amount of ammonia employed and temperature of digestion, it is necessary to use special precaution, and to control the temperature carefully.

There is no doubt that the character of the gelatine employed exercises a considerable influence on the resulting emulsion. Capt. Pizzighelli pointed out to me that, while one sample of gelatine will stand digesting for fifteen minutes with ammonia at a temperature of 70° C., another will produce a foggy emulsion if a temperature of 50° C. be employed.

The relative effect of ammonia is due to its state of concentration, and in calculating the amount necessary in an emulsion, due regard must be had to this point, and not to the proportion of bromide of silver contained. Bromide of silver will derive considerable advantage from a dilute ammonia, which would infallibly fog if a more concentrated sample were employed, especially when the silver is warmed in presence of gelatine. Monckhoven[1] was the first to communicate his studies on the influence of ammonia in the preparation of a gelatine emulsion, and to point out that the increase of sensitiveness was due to the conversion

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[1] *Photo. Corr.*, 1879, xvi., 160-200. Johnson also communicated in the *Brit. Jour.* Almanac for 1877, p. 95, the method of treating a gelatine emulsion with ammonia (*Photo. Mitth.*, 1879, xvi., 229); but as he did not recognize the true effect of ammonia on bromide of silver, we must credit Monckhoven with the priority of discovering this method of emulsification.

of the flakey bromide of silver into the granular modification, and I have clearly corroborated the truth of this statement. Ammonia has a favourable effect when used cold, but I have been unable to detect any change in the molecular condition of the bromide of silver. Carbonate of soda, on the other hand, has an equally favourable effect on a cold emulsion, but it produces no molecular change when heated or when digested with warm water.

If a gelatine emulsion containing 1¾ per cent. ammonia be digested at temperatures varying between 14° C. and 20° C., the conversion into the sensitive modification is exceedingly slow; and even if the operation be continued for eight days, the films still transmit a small quantity of red light. At 35° C. or 40° C., the change proceeds gradually, and is completed in about one or two hours; the presence, however, of a small quantity of soluble bromide retards the operation for six or eight hours. At all events, an hour's digestion under the above circumstances produces as rapid an emulsion as several days by the low temperature methods. If the temperature be raised above 50° C., the change is hastened a good deal, but the emulsion is liable to fog; and if a temperature as high as 60° C. or 100° C. be employed, the operation is exceedingly rapid, but decomposition is certain to set in, and especially in the latter case. If ammonia be employed, the temperature should never be allowed to rise above 40° C. A gum emulsion containing 6 per cent. ammonia remains unchanged at the end of twelve hours' digestion at 15° C. or 20° C.; at the end of twenty-four hours it is rather more sensitive, and in four days the change into the granular modification is very nearly complete, though the films still transmit a little red light. We have, therefore, every reason to infer that increase of temperature is, under all circumstances, a powerful agent in converting bromide of silver into its most sensitive condition, and especially so in the presence of ammonia; but, at the same time, we must bear in mind, that if an emulsion is to be digested at a high temperature, it is impossible to employ so large a proportion of ammonia as 6 per cent.

The sensitive condition of bromide of silver is most easily attained by mixing potassium bromide with an ammoniacal solution of silver nitrate. The first experiments in this direction were made by Captain Pizzighelli, in April, 1880. He worked with the ordinary proportions of gelatine, bromide, and silver; but he added to the silver nitrate, dissolved in water, sufficient ammonia to redissolve the precipitate originally present, and leave the solution clear. The potassium bromide is dissolved in the swelled gelatine over the water bath, and, when it has cooled to 30° C., the ammoniacal solution of silver is added. The conversion of the bromide of silver takes place even more rapidly than when an emulsion is boiled without ammonia, owing, most probably, to a combination, in the first instance, between the bromide of silver and the ammonia. The change always occupied a few minutes, but was generally complete in a quarter of an hour or twenty minutes, even when the temperature was allowed to sink during the time to 25° C.

The resulting films were grey by transmitted light, highly sensitive, and gave brilliant negatives. The temperature of the gelatine on the introduction of the ammonio-nitrate of silver should not exceed 40° C., otherwise decomposition and chemical fog ensue. The effect is still more rapid if the operation be reversed, and the silver nitrate added to the gelatine contained in an ammoniacal solution of potassium bromide, and appears to take place instantly on the addition of the silver being made. These methods of producing sensitive emulsion are very convenient, as so little apparatus is required.

If the ammonia be added to the emulsion after the bromide of silver is formed, the same degree of sensitiveness can only be reached by a more prolonged digestion. As this circumstance renders both the gelatine and the bromide of silver liable to decomposition, any method which makes the operation safer, as well as saves time, will be welcome.

Another reason for the increase of sensitiveness caused by ammonia is the fact that this body, although it may be removed by washing previous to exposure, still leaves an alkaline reaction.

If, as Rammelsberg states, ammonia is not absorbed by bromide of silver, still every trace of free acid, which can do any harm, is removed.

Such free acids are not present in the best samples of gelatine, but are produced by the silver nitrate and potassium bromide, and are spontaneously developed in inferior samples of gelatine. Carbonate of soda in small quantities is generally admitted to have a beneficial effect on an emulsion; if the proportion be too large, chemical fog is the result.

Be the causes what they may, there is no doubt about the value of ammonia in regard to sensitiveness; and, personally, I believe that the formation of the sensitive modification of bromide of silver depends upon and varies with the solubility of the latter in ammonia.[1]

The results of the numerous experiments that I have made with emulsions generally have led me to believe that it is useful to treat a gelatino-bromide emulsion with ammonia, after heating. Not only is any trace of acid removed, but there is the opportunity of remedying any failure of conversion into the sensitive condition which may have occurred during the operation. In this way the sensitiveness can be increased either more or less without affecting the other qualities of the emulsion. I have published this result before, and am convinced that ammonia employed in this manner, or else with a cold emulsion, gives as great a sensitiveness as is attained by digesting for two hours at a temperature of 37° C.

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[1] Bathing the plates in a cold aqueous solution of ammonia also heightens their sensitiveness.

It is worth noting that an addition of from 3 per cent. to 10 per cent. ammonia operates on a collodio-bromide emulsion in the same manner as on a gelatino-bromide emulsion, namely, by producing the green modification, and its consequent increase of sensitiveness. Under favourable circumstances the sensitiveness is about doubled. As ammonia only operates in the presence of an excess of soluble bromide, collodion emulsions so treated are only about one-tenth to one-twentieth as sensitive as corresponding gelatine emulsions; and, in my experience, the use of an organifier does not reduce this difference.[1]

It is evident that these facts only apply in the absence of silver nitrate, as the latter is decomposed by alkalies with the formation of silver oxide, and foggy pictures are produced on development.

Organic Substances Absorbing Bromine.

According to Vogel, such bodies as gelatine, tannin, gallic acid, morphia, resin, and catechu, exercise a favourable influence on bromide of silver in presence of an excess of soluble bromide; but in the presence of an excess of silver they have no sensitizing action. My experiments have decided this in the case of collodion, and I may summarize the results as follows. An organic substance exerts an accelerating action on sensitiveness, so long as no other body is present acting in the same direction. In the case of a gelatino-bromide emulsion, gelatine acts as an organifier, and, therefore, no other is required; but, in the case of collodio-bromide, such substances as tannin, morphia, &c., double the original sensitiveness. If the second sensitizer or organifier be much more powerful than the first, its effect is very small. Dr. Vogel quotes the action of pyrogallic acid on gelatine emulsion in supporting this.

In all cases the direct envelopment of bromide of silver in a

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[1] Ammonium carbonate is less energetic than pure ammonia; the emulsion may be boiled, in fact, without inducing fog.

substance easily oxidised is very favourable to sensitiveness. Collodio-bromide emulsion, prepared with excess of silver, is much less sensitive than a gelatine emulsion containing an excess of soluble bromide; and yet nitrate of silver is a better sensitizer than gelatine, as I have proved by comparing a collodion emulsion sensitized with silver nitrate with another sensitized—or, rather, organified—with gelatine in the presence of an excess of soluble bromide. Resinous emulsions, or collodion emulsions containing much resin, should be highly sensitive, as here the particles of bromide of silver are closely enveloped in a sensitizer.

In this case the employment of ammonia is recommended as a means of producing the sensitive modification, as little is to be gained by boiling alcoholic solutions.

No good reason has ever been discovered to account for the preponderating sensitiveness of bromide of silver when contained in gelatine, for while it is equally possible to produce the fine granular description in collodion, it is, when contained in this vehicle, less sensitive than the powdery form, and far less so than the granular, when contained in gelatine. An attempt has often been made to explain, as a reason of inferior sensitiveness, the slight porosity of the collodion film as compared with a gelatine. This is entirely insufficient, as while the latter is much more easily impressed by the actinic rays, it offers more resistance to the action of a pyrogallic developer prepared with alcohol, than does a collodion film.

Optical Sensitizers or Organifiers.

These bodies, mostly in the form of dyes, which increase the sensitiveness of bromide of silver to certain rays of the spectrum, have an important bearing on collodion emulsions. Certain aniline dyes, according to Vogel, render gelatine plates sensitive to the orange and red rays; but their effect on collodion plates is more remarkable.[1] Do not good gelatine plates, without any adventitious aid, possess a special sensitiveness to such rays?

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[1] *Phot. Mittheil.*, 188, xvii., 15.

IV.—EFFECT OF TEMPERATURE ON THE FORMATION OF THE LATENT IMAGE ON BROMIDE OF SILVER PLATES.

Variations in temperature between 5° C. and 25° C. seem to have no effect either on the decomposition of bromide of silver plates under the action of light, or on the formation of the latent image, so long as one and the same temperature prevails after exposure and during development. In reference to the formation of a visible image, Bunsen and Roscoe have found that variations of atmospheric temperature or moisture have no effect on the rapidity with which paper coated with chloride of silver darkens under the action of light.

V.—RESULTS OF USING GELATINO-BROMIDE PLATES WET.

Gelatine plates used wet only prove from one-fifth to one-sixth as sensitive as when dry. Not only is the chemical effect of light reduced by its passage through a medium of water, but the surface of a wet gelatine film is much rougher and more unequal than in a dry state. We can quite understand, therefore, why it is that gelatine plates used wet give pictures wanting in definition.

Collodion films, when wet, do not show the same defect as gelatine plates under the same treatment. In fact, collodion plates are superior in this state, owing, probably, to the fact that the pores of the film are more open than those of a gelatine plate freshly wetted.

It is characteristic of gelatine bromide plates that they are more opaque when wet than when dry; while in the case of collodion emulsion, the reverse obtains. This remark applies to the undeveloped film only; the developed picture is much the same when dry as when wet.

VI.—EFFECT OF COLOURED RAYS ON GELATINO-BROMIDE OF SILVER.

The relative effect of different rays of the spectrum on the various modifications of bromide of silver has been studied by Monckhoven. A freshly-prepared emulsion containing bromide of silver in its powdery condition is sensitive between the lines M and F, that is, nearly up to the green. By prolonging the digestion considerably, an emulsion of extraordinary sensitiveness is produced, containing bromide of silver in its fine granular condition, the sensitiveness of which lies between the ultra-violet at one end of the spectrum, and the ultra-red at the other. These facts fully confirm the theory that photo-chemical decomposition depends on optical absorption. The relative increased range of sensitiveness to coloured rays becomes evident in proportion to the absolute sensitiveness of the compound to white light.

VII.—QUALITY OF CHEMICAL DEVELOPERS, AND THEIR INFLUENCE ON THE SENSITIVENESS OF BROMIDE OF SILVER.

Since the production of a picture by chemical development depends on the invisible reduction of the bromide of silver, as well as on the operation of the developers, it is evident that the physical condition of the bromide of silver, as well as that of the developer, are functions of sensitiveness. I may give the results of my investigations,[1] which were fully published, a short time ago, in a few words. Shortness of exposure depends on the reducing action,[2] as well as the state of concentration of the

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[1] *Photo. Corr.*, 1879, xvi., 223, 248; and in my pamphlet, "Comparison of the New Ferrous Oxalate Developer with Alkaline Pyrogallic Acid.' Vienna, 1880.

[2] The reduction of exposure by increasing the strength of the developer has its limits, in the fact that bromide of silver which has been insufficiently exposed will discolour, and no image will be developed.

developer employed. Warming the developer to 15° C. or 20° C. permits of a shorter exposure. Comparative experiments on the sensitiveness of the silver haloid salts should be made with the same developer.

Accurate researches into the behaviour of the various modifications of bromide of silver in the presence of a chemical developer prove that the reduction of the former, when prepared with an excess of soluble bromide, is more rapid than when an excess of silver is present; and that an emulsion which transmits orange light, and contains the powdery modification of bromide of silver, is less easily acted on than one containing the so-called green modification, which transmits blue light. In all cases the free bromide was carefully removed by washing, a point which, as is well known, affects the sensitiveness as well as the capacity for reduction under the developer, and the resulting plates developed clear and free from fog.

We may conclude, therefore, that gelatine emulsions which transmit red light, owing to insufficient digestion, not only are less sensitive, but are also very slowly reduced either by ferrous oxalate or weak alkaline pyrogallic acid, the result being inferior, hard negatives, while the developer has not sufficient energy to bring out an insufficiently-exposed picture. Such emulsions are not only the better for, but require, a powerful pyrogallic developer, as ferrous oxalate is of little use under the circumstances.

An extremely sensitive emulsion does not require so powerful a developer. A weak ferrous oxalate solution quickly develops a soft, harmonious picture, while the more powerful pyrogallic developer, necessary in the cases previously mentioned, brings about a rapid decomposition of the bromide of silver, and gives fog without any previous exposure of the plate to light.

This treatment, on the other hand, with ferrous oxalate is, to a certain extent, characteristic; for, if a gelatine emulsion developed by my formula for ferrous oxalate without bromide of ammonium yields hard, glassy negatives, there is every reason to conclude that the emulsion has been insufficiently washed, or that it contains the insensitive modification of bromide of silver. This conclusion can be justified by examining the plate by transmitted light.

Developers[1] warmed to over 30° C. are extremely rapid in their action, and generally induce fog. I believe that any attempt to develop collodion plates with warm developers would be useless, owing to their liability to fog the plate. We have another method, which I consider preferable, of accelerating the action of the pyrogallic developer—that of adding ammonia.

The use of warm solutions in the development of gelatine plates cannot be taken into consideration, owing to their solvent action on the gelatine film.

VIII.—ELECTROLYTIC ACTION DURING DEVELOPMENT.

If a plate be coated with a film of emulsion three or four times as thick as is necessary to ensure the complete absorption of the chemical rays, I have remarked that the reduction of the bromide of silver takes place throughout the whole thickness of the film. It would have been impossible for the light, even had it been much more powerful, to have produced such an effect. I was therefore led to the conclusion that the further reduction was caused by an electrolytic action between the ferrous oxalate and the silver previously reduced on the surface of the film under the action of the developer. As a means of confirming the accuracy of this conclusion, I laid a piece of clean silver wire on a bromide of silver film in the dark, and then developed the same with ferrous oxalate, the result being a reduction of silver

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[1] Carey Lea, as well as Trutat, have recommended the employment of warm solutions of alkaline pyrogallic for collodion emulsion plates; and in 1861 Simpson observed that the effect of increasing the temperature of a neutral pyrogallic solution was to cause a greater rapidity of development.

where the wire had been in contact. Abney's[1] experiments on this point confirm the theory of electrolytic decomposition, for if a developed picture consisting of metallic silver be coated with gelatine emulsion, and then treated with a developer, the bromide of silver, without any previous action of light, becomes reduced by simple contact to the metallic state on the corresponding parts of the film, and the picture becomes thereby reproduced.

We may infer, in regard to the behaviour of bromide of silver —particularly in presence of gelatine—during development, the following practical conclusions :—

1. That a secondary electrolytic action occurs readily during development, acting not only downwards, but also laterally. For instance, as I believe Abney first pointed out, black lines on a white ground appear to contract. I have proved this fact further by careful microscopical measurement.

2. Under-exposed pictures in which a long time elapsed between the appearance of the highest lights and the deepest shadows must, of necessity, be hard and over-intense. The high-lights first developed increase rapidly to complete opacity before the shadows have acquired the least vigour. These facts are familiar to all, but may be remedied if an attempt is made to develop the various parts of the picture in rapid succession; a result to be obtained either by increasing the sensitiveness and the capacity for reduction of the bromide of silver, or by adding to the energy of the developer. I recommend the former of the two as being the best in practice, especially in portraiture.

Quite recently, Captain Abney has suggested the use of a small quantity of iodide of silver in an emulsion as a means of checking the excessive reduction of silver, since he argues that the former, being incapable of itself of reduction under the action of the developer, keeps the particles of bromide of silver

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[1] "Emulsion Processes in Photography." London, 1878, page 11.

asunder, and breaks up their actual continuity. By this means, he contends that the excessive vigour brought about by the electrolytic action previously described may be avoided. This advantage appears to me to be problematical, and does not sufficiently counterbalance the disadvantage of such a proceeding. For myself, I prefer to employ a simple bromide of silver emulsion, which is easily reduced, extremely sensitive, and gives a soft and brilliant picture. If the development be prolonged, either owing to the quality of the emulsion or to the excessive use of bromide, hard negatives are the result.

MECHANICAL PRESSURE.

Carey Lea has pointed out that the effect of mechanical pressure on iodide of silver is such, that when wet plates followed by acid development are employed, metallic silver, in its nascent state, often becomes attracted in the same manner as if the plate had been previously exposed to light. I have made repeated observations in this direction, not only with iodide, but also with bromide of silver, coupled with physical development.

If a piece of clean glass be pressed in contact with a plate sensitized in the silver bath, the part which has been subjected to pressure will, on treatment with acid, iron, and silver, attract a deposit of metallic silver. But in the case of dry-collodion plates similarly treated, no such action seems to result, nor is it apparent in the case of gelatino-bromide of silver followed by physical development.

X.—ALTERATIONS IN BROMIDE OF SILVER ANALOGOUS IN THEIR EFFECT TO THE ACTION OF LIGHT.

Bromide of silver exposed to light for an infinitesimally short space of time evinces a greater disposition to reduction under the action of a chemical developer, than that which has been absolutely protected from light. The theory that bromide of silver is converted during exposure to the sub-bromide by the liberation of bromine, is now generally accepted. Sutton's hypothesis, that the latent image consists of silver oxybromide ($AgBrAg_2O$), is entirely untenable, in consequence of Abney's experiments, which indicate that a latent image consisting of iodide or bromide of silver is not only capable of formation in the absence of an acid, but that in presence of the latter the power of development is destroyed by oxidation. Analytical results leave no room for doubt that the chemical composition of bromide of silver, which, in other respects, is apparently unchanged, remains constant.

By special treatment, pure bromide of silver can be made to offer the same easy disposition to reduction, without insolation, as is characteristic of the (so-called) latent action of light. If bromide of silver prepared with a small excess of soluble bromide[1] be digested under heat for a day, in presence of a body having a slight reducing action, it will be found to fog under the action of a chemical developer, as readily without as with exposure to light. Gelatine exercises a weak reducing action, a fact familiar to all who have employed it in connection with any of the salts of silver according to various photographic formulæ. Bizzio discovered, some time ago, that glue exercised a reducing action, not only on salts of silver, but generally. He found, for instance, that mercuric chloride in the presence

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[1] This change takes place more rapidly in the case of bromide of silver prepared with excess of silver nitrate, washed, and then emulsified in gelatine. Abney considers that, in the case of a collodion emulsion prepared with excess of nitrate of silver, the image is formed of sub-silver bromide, and that the following reaction takes place:—

$$2AgBr + AgNO_3 = AgBr + Ag_2Br + NO_3.$$

The proof of this reaction, which appears highly improbable to me, is not evident. It is quite likely, in this case, that a simple reduction of silver nitrate to the metallic state takes place, and that the silver so reduced produces the darkening of the bromide of silver under the action of the developer.

of an aqueous solution of glue becomes converted into mercurous chloride, and that mercuric oxide in the presence of an alkaline solution of glue becomes reduced to the metallic state.

If a gelatino-bromide of silver emulsion, prepared with a small excess of soluble bromide, be heated for about ten days, at temperatures ranging between 30° C. and 50° C., or for a shorter time at from 60° C. to 90° C., the silver is reduced as easily in the presence of a developer, without any previous exposure, as would occur in the case of a normal emulsion exposed for several seconds, or even minutes. Moreover, there is no change in colour apparent to account for so considerable a reduction. Captain Toth and myself made use of the proportions of bromide of potassium and silver nitrate previously given, to determine more accurately the relative effect of length of digestions and temperature on the spontaneous decomposition of gelatine bromide emulsions. At 30° C. and 40° C. fog commenced at periods ranging from six to twelve days, and when a temperature of 100° C. was employed, developed to a very considerable extent in from three-quarters of an hour to one hour and a quarter. In these experiments neutral salts, and gelatine having a slightly acid reaction, were employed. These results do not necessarily obtain in the case of all samples of gelatine, as some may be digested for longer periods without damage.

Collodio-bromide emulsion will remain free from decomposition under the action of heat, clearly so long as the pyroxyline does not act as a reducing agent; but directly tannin or gallic acid is added, and the emulsion allowed to stand at ordinary temperatures for about a month, spontaneous decomposition sets in, causing fog under the action of the developer. The same effect is apparent when bromide of silver is heated for a shorter time in presence of an alkali. Small quantities of sodic or calcic carbonate, added until an alkaline reaction is obtained, materially hasten the change. Gelatine emulsions which have been heated for twenty-four hours at temperatures between 30° C. and

40° C., with one and three-quarters to two per cent. of ammonia, turn out very foggy ; after six hours' digestion at 60° C. or 70° C. an emulsion is entirely ruined. If the temperature be raised to 100° C., decomposition sets in at once, and an emulsion boiled with ammonia is equally useless.

Should a gelatine emulsion be prepared entirely in the presence of an alkali, or in that of a weak acid, it is equally necessary to take into consideration the alkaline or acid reaction of the gelatine itself. An acid gelatine does not act injuriously on bromide of silver if boiled for a short time ; but an alkaline reaction under similar circumstances readily conduces to fog. In the case of the cooking process, or in that of Bennett, which requires prolonged digestion, the accidental presence of an alkali may cause a good deal of trouble. In the latter process we must use an acid gelatine which develops no ammoniacal fumes, even after ten days' digestion ; but if the gelatine have an initial alkaline reaction, these fumes will probably be given off in from two to four days' digestion. An alkaline gelatine, and an alkaline sample of potassium bromide, need not necessarily be injurious if the ammonia be added intentionally, and the whole operation be suitable to an excess of alkali. It is an exceedingly interesting fact that all bodies which retard the formation of the latent image are analogous in their operation to substances having a weak fogging action during the process of digestion. Potassium bromide, for instance, in proportion to the excess in which it is present, retards the latent action of light ; and in the preparation of an emulsion with prolonged digestion this body, either alone or in the presence of ammonia, gives a greater tendency to fog if present in large quantities than if present in smaller quantities.

XI.—COMPARISON OF THE SENSITIVENESS OF BROMIDE OF SILVER WITH THAT OF IODIDE AND CHLORIDE OF SILVER IN CONNECTION WITH CHEMICAL DEVELOPMENT.

Iodide of Silver.

It has long been known that iodide of silver prepared with excess of iodide is almost entirely insensitive. If prepared with excess of silver, it is less sensitive than bromide of silver similarly prepared; and in addition to requiring, when chemically developed, about five times as much exposure, gives very thin negatives. These facts, of which many are ignorant, are very remarkable, as when physical development is employed, iodide of silver is more sensitive than either bromide or chloride of silver.

Mixtures of Bromide and Iodide of Silver.

The result of an addition of iodide of silver to bromide is to make it less sensitive than pure bromide of silver, and although the process has often been suggested, it is not always to be recommended. If the proportion of iodide of silver—either in a collodion or a gelatine emulsion—be considerable, as compared with the bromide, it exerts an equally unfavourable action. Gelatino-bromide of silver containing either 25 or 50 per cent. of iodide of silver, turns out very insensitive, and gives very thin negatives. If only 10 per cent. of iodide be employed, and the emulsion be digested at a lower temperature in presence of ammonia, the result is inferior to one prepared with pure bromide of silver. Still, an emulsion cooked for half an hour is very sensitive. However, an emulsion containing iodide has the advantage of being less liable to decomposition, owing to the restraining action of iodide of silver. According to my experience, the addition of one-twelfth of iodide reduces the sensitiveness a little, gives thin negatives, and prolongs the time of development. The latter peculiarity is incidental to all forms of bromide emulsions which have been insufficiently converted into the sensitive condition. I may call attention, however, in connection with this point, to the fact that slow development does not necessarily depend upon the sensitiveness, or otherwise, of a film in presence of light.

According to Abney,[1] an emulsion containing $\frac{1}{8}$ of iodide has a range of sensitiveness from the violet end of the spectrum as far as the line E, or to about the end of the green; with $\frac{1}{12}$ iodide it is sensitive as far as D, the end of the yellow; and with $\frac{1}{24}$ iodide as far as B, the orange. The most sensitive compound is, of course, pure bromide of silver, which is sensitive to the red rays, and the less the proportion of iodide to bromide present, the more sensitive is the result.

The idea prevails that a greater sensitiveness to the coloured rays affects a general sensitiveness to white light containing the usual illuminative rays. I have not allowed this idea to influence my judgment, although I believe there is reason for supporting it. In fact, Schultz-Sellack has pointed out that the light reflected from shadows is especially poor in violet rays. Objects which are more illumined by the visual than the chemical rays are abundant in nature. Consequently, the ideal of photography should be a preparation which, as in the case of the human eye, is more sensitive to the red and yellow than to the blue and violet rays, and gives the natural effect of the illumination. Above all preparations, pure bromide of silver comes nearest to these requirements.

Is the advantage of clearness in the shadows, claimed for a bromo-iodide emulsion, peculiar to this modification alone? I think not, and there is no doubt that by the unsparing use of potassium bromide, a plate consisting of pure bromide will develop very clean in the shadows. I certainly think that the superior advantages of pure bromide of silver, consisting in quick deve-

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[1] *Photographic News*, 1880, xxiv., 196

lopment combined with a greater range of sensitiveness, as well as general sensitiveness to white light, are sacrificed in the employment of one containing iodide of silver, which does not possess these advantages. That it can be developed in a less trying light is true; but the light which it requires approximates in no way to that customary in the case of wet plates, where a more or less yellow glass transmitting a good deal of green light is available.

On the above grounds I have expressed the opinion that for ordinary purposes it is better to adhere to bromide of silver alone; but I doubt not that the points which I have suggested as undesirable in the case of a bromo-iodide emulsion may, under special circumstances, be the reverse; and that the softer contrasts, and possibly the decrease of sensitiveness, may be, for many purposes, arguments in its favour. The fact that bromo-iodide of silver permits a greater latitude of exposure, and does not fog so readily under careless development, will be welcome to many landscape photographers, who, as a rule, do not care for instantaneous exposures. An emulsion containing $\frac{1}{10}$ of iodide, and boiled for half-an-hour, is generally some five to six times as sensitive as a wet plate.

To complete the subject, I give Abney's latest method of preparing a bromo-iodide emulsion.[1]

1.—Iodide of potassium	15	grammes
Bromide of ammonium ...	120	,,
Gelatine	30	,,

are dissolved by heat in 480 c.c. of water, and the temperature brought up to about 53° C.

2.—Silver nitrate	216	grammes
Water	480	c.c.

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[1] Abney on "The Practical Working of the Gelatine Emulsion Process." London, 1880, 20. According to his last researches, iodo-bromide emulsion is more sensitive than pure bromide, an opinion opposed by Vogel.

No. 2 is then gradually introduced, and the emulsion is left in boiling water for twenty to thirty minutes.

After this, 160 grammes of gelatine, previously swelled in water, are added. The addition of ½ gramme of chrome alum may be desirable. Lastly, 60 c.c. of alcohol is added, and the emulsion filtered.

Chloride of Silver.

This body is extremely sensitive, and, in this respect, ranks close to bromide of silver.[1] My experience, so far as it has gone, enables me to state that as the former is even more liable than bromide of silver to spontaneous decomposition under the action of a powerful solution of alkaline, pyrogallic, or ferrous oxalate, its development is attended with some difficulty. When prepared with excess of silver, it is more sensitive than when prepared with excess ef chloride; but, like bromide of silver under similar circumstances, it is liable to irregular development.

Mixtures of Chloride and Bromide of Silver.

I must, in regard to mixtures such as the above, offer an opinion in opposition to that generally expressed in photographic journals. I cannot think that such an addition is to be recommended, owing to the want of harmony of the constituents in presence of a chemical developer.

Chloride of silver fogs entirely before the bromide is reduced in the lighted portions of the picture.

A gelatino-bromide emulsion containing chloride is generally not more sensitive than one containing bromide alone. Fog always makes its appearance if the ordinary developers be em-

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[1] Berkeley arrives at the same result by an independent method. He believes that sodic hydrosulphite can be employed with success as a developer for chloride of silver (*Photo. News*, 1880, xxiv., 233).

ployed. The addition of soluble chloride has not a sufficient restraining action. Potassium bromide, plentifully used, will retard fog, and give clear negatives, owing to the fact that in the presence of this substance chloride of silver is converted into bromide of silver.

As regards a chloro-bromo-iodide emulsion, my experience is not favourable. Generally, I think it is a mistake to combine substances together whose behaviour in presence of a developer is dissimilar, for a developer which is suitable to one of the components may be entirely unsuitable to another. A developer, for instance, which operates most successfully on bromide of silver, will be found too weak for iodide of silver, and too powerful for chloride of silver.

CHAPTER III.

BEHAVIOUR OF GELATINE IN EMULSIONS

I HAVE directed my investigations towards the solution of various important questions connected with this subject, and the results will be found embodied in the following chapter.

I.—MELTING AND SETTING POINTS.

In the preparation of gelatine emulsions a knowledge of these points is important. I have gone into the subject before in my work, "The Reactions of Chromic Acid and Chromates on Gelatine," to which reference may be made. The investigations were made with ten different kinds of gelatines, including collotype gelatines by Coignet, Heinriches, Creutz, Nelson, Fischer und Schmidt, &c. The determination of the setting points, which Dr. Lohse has already indicated in the case of one sample, is a matter of some difficulty, as the mere passage of the fluid into the gelatinous state is not sufficient to fix it.

The setting and melting points are tabulated below.

Solution.	Gelatinizes at °C.			Melts at °C.			Sets at °C.		
	Minm.	Mean.	Maxm.	Minm.	Mean.	Maxm.	Minm.	Mean.	Maxm.
4 p.c. ...	16·9°	22[illegible]	25·1°	25·2°	28·8°	30·5°	15·2°	20°	23°
10 p.c....	17	24·2	28	31	32·5	33·6	16	22·8	26

The results in this table show that generally the melting point of gelatine is some 8° or 10° higher than the complete setting point, and further, that the more gelatine an emulsion contains, the higher is the temperature at which it melts and sets. It is worth noting that the setting points of different samples of gelatine differ to the extent of 8° or 9° C., and the same with the melting points. Consequently, in selecting gelatine for any purpose, these facts should be borne in mind.

II.—Addition of Alum or Chrome Alum to Gelatine.

These bodies have an influence not only on the general behaviour of gelatine, but also on its setting point. A 4 per cent. solution of gelatine, to which chrome alum to the extent of 5 per cent. of the weight of dry gelatine has been added, gelatinizes readily. The setting point is 1° to 2° C. higher than if ordinary alum be added. Once set, gelatine containing chrome alum requires a temperature as high as 60° C. or 70° C. to melt it. The dried film no longer swells in water. Gelatine emulsion containing chrome alum must be treated with care, and requires the addition of a small quantity of glycerine to facilitate the introduction into the film of the developer. When the gelatine requires hardening, ·05 to ·1 gramme chrome alum may be added to every 100 c.c. of the emulsion—or, better, to 500 parts of emulsion add 5 to 6 parts of the following chrome alum solution :—

Chrome alum	20	parts
Water	450	,,
Glycerine	200-240	,,

An emulsion containing chrome alum should be all used up at once. Ordinary alum proves much less energetic. If a 4 per cent. solution of gelatine contains alum in the proportion of 5 per cent. of the weight of the dry gelatine, the setting point becomes raised by 1° or 2° C., and the melting point about 10° C.;

but a solution containing ordinary alum, when once set, will melt again entirely if exposed to heat. An addition of 15 per cent. raises the setting power some 5° to 6°, the mean being about 25° C. to 26° C., and the melting point is raised about 15° to 20°, or to about 45° C. An addition of 30 per cent. increases the setting point to 33° C., and the melting point to about 48° C.; but even so large a proportion as this does not prevent gelatine from remelting when exposed to heat. Gelatine containing 15 per cent. of alum has still a tendency, though considerably reduced, to absorb water, and even 30 per cent. of alum does not destroy this power entirely.

In ordinary, alum will be found a useful agent for raising the setting power, as well as increasing the hardness of a too soluble sample of gelatine. An addition of alum to the extent of 10 per cent. of the gelatine emulsion can be employed without injury; but glycerine must be added to facilitate the action of the developer.

A sample of gelatine which proves too soft may be improved by the following method. To every 100 c.c. of the emulsion add 3 to 6 c.c. of the following solution:—

Water	50 parts
Alum	4 „
Glycerine	4 „

The quantity required varies, of course, with different samples of gelatine. A few drops of the solution are often sufficient.

III.—CHANGES PRODUCED IN GELATINE BY HEATING AND PUTREFACTION.

In the chapter relating to the behaviour of the haloid salts of silver in emulsion, I remarked on the changes produced in a gelatine emulsion by digestion, without, however, alluding to the changes which the gelatine itself undergoes during the operation.

These changes, so far as I have been able to determine, are as follow:—

1. Hoffmeister has proved by experiment that gelatine during prolonged digestion splits up into two substances—semi-glutin ($C_{55}H_{85}N_{17}O_{22}$), insoluble in alcohol, and precipitated by platinic chloride, and hemi-colline ($C_{47}H_{70}N_{14}O_{19}$), which is soluble in alcohol and not affected by platinic chloride. Semi-glutin, by standing, reduces silver nitrate without precipitating it, while hemi-colline causes a flaky precipitate of the same. This splitting up of the gelatine is the reason why gelatine after long-continued boiling loses its setting power, without, however, any decomposition setting in. The latter is only apparent after several days' boiling, and renders the gelatine quite fluid; but boiling for a half, or even an hour, does not produce an injurious effect.

2. If gelatine be submitted for a long time to a temperature of 30° C. to 50° C., it loses equally its setting power; but at a later period than in the former case. It is very difficult to decide the exact point when putrefaction, shown by the development of gas and formation of ammonia in combination, begins, and the separation above alluded to ends.

3. Boiling with even a slight addition of ammonia, or of acid, quickly deprives gelatine of its setting powers, and the same splitting up appears to occur; at all events, the formation of hemi-colline is apparent. Gelatine warmed with water containing 1 or 2 per cent. of ammonia, at a temperature not exceeding 40° C., will, at the end of three hours, be found to have the temperature of the setting point lowered to 1° or 2°. A 4 per cent. solution of gelatine digested for five minutes with a 2 per cent. aqueous solution of ammonia at temperatures of 30° C. or 40° C., has its setting power reduced from 5° to 8° C., and after three hours' digestion, about 1° C. to 2° C. If a sample of gelatine is too soft, alum can be used to harden it.

The fixed alkalies have the effect of decomposing the gelatine when boiled with them; and acid potassium bromide—as might have been expected—deprives gelatine of its setting power more rapidly than a neutral sample.

4. This loss of setting power, caused by heating at 30° C. or 40° C. for a long time, is almost always the result of decomposition. Germs of putrefaction are always present in the atmosphere, so that no artificial ferment is necessary. Decomposition is very quickly set up by the addition of a small quantity of animal tissue—for instance, muscular tissue, or, still better, the substance of the pancreas, and digesting over heat. According to Weyl, the products of decomposition caused by water and pancreas are alike.

In their re-action, according to Nencki, there are formed from every 100 parts of gelatine, 9·48 parts of ammonia, 24·2 parts of volatile fatty acids, 12·2 parts glycal, 19·4 parts peptone, and 6·45 parts carbonic acid. The volatile fatty acids are acetic, butyric, and valerianic acid, the first of these being more abundantly present in proportion as the process of decomposition is prolonged. The gas given off does not consist of carbonic acid alone. The ammonia is combined with the fatty acids and remains in solution.

Jeannert points out, in 1877, that putrefaction occurs in a gelatine solution contained in a close vessel, although, under such circumstances, it takes about six times as long to develop as when the solution is in contact with the atmosphere. The organisms produced during the progress of decomposition are anœrobes, which are capable of spontaneous generation, and can exist apart from contact with the air. Dr. Lohse's recent investigations bear on this point.

Gelatine which has been subject to decomposition produces fog in gelatino-bromide plates.

IV.—Occurrence of Decomposition in Different Samples of Gelatine.

In order to obtain an insight into the process of decomposition in various kinds of gelatine when heated at temperatures between 30° C. and 40° C., I induced Herr Richt to undertake a series of experiments. For this purpose, twelve different sorts of gelatine were submitted to the conditions above described. He took these different gelatines from samples by Nelson, Heinrichs, Creutz, Coignet, Fischer und Schmidt; the remainder were of unknown manufacture. I may mention, to begin with, that the initial reaction varied in the different samples. The gelatines of only two separate manufacturers were alkaline; the remainder were distinctly acid. This point is of importance, because on it depends the development or otherwise of free ammonia during long-continued heating.

1. Nelson's No. 1. Initial reaction alkaline. Ammoniacal fumes developed after three or four days' digestion, and rapidly increased.

2. Nelson's No. 2 same as No. 1.

3. Nelson's No. 3 same as Nos. 1 and 2.

4. Fischer und Schmidt's emulsion gelatine. At first, slightly acid reaction. At the end of three days, gave off free ammonia like Nelson's gelatines.

5. Fischer und Schmidt's collotype gelatine. Initial reaction slightly acid. At the end of nine days, gave off ammonia.

6. Heinrich's collotype gelatine (mark W. H.). Acid at first. At the end of a fortnight's stewing, gave no signs of free ammonia.

7. Heinrich's softer kind. Reactions same as in the previous instance.

8. Creutz' gelatine (mark F. C. F.). A firmer kind, giving a yellow film. Reactions same as those of the two former numbers. Remains acid after fourteen days' digesting.

9. Creutz' softer or more opaque sample, giving a white film. Reactions same as in the last.

10. Coignet's. Reactions, as in previous cases; remains acid.

11. Manufacture unknown. White and very fine gelatine. Initial reaction acid, and remains so after fourteen days' digestion.

12. Manufacture unknown; white, and very fine gelatine; continues to have an acid reaction.

In our experiments, therefore, only those gelatines which had at first an alkaline reaction gave ammoniacal fumes after long-continued cooking; those whose reaction was at first distinctly acid showed no sign of free ammonia, even after fourteen days' digesting, and the experiments we carried no further than this. In one case only a gelatine which had at first a slightly acid reaction lost it after nine days' stewing, and then gave off ammonia. We also proved that a gelatine which had been fined with a large quantity of egg albumen turned alkaline much quicker, and lost its power of setting much sooner than if it had received no such addition. I cannot, consequently, recommend addition of albumen for clearing gelatine.

We can thus see that after a gelatine bromide emulsion has been digested for several days at a temperature of from 30° C. to 40° C., ammonia will be developed if an alkaline gelatine has been used. Now, as we know, ammonia on the one hand stimulates the sensitiveness, but, on the other, promotes the decomposition of the emulsion; hence those sorts of gelatine which have an alkaline reaction should only be employed with the greatest care, when the emulsion is to be cooked a long time, especially as there is no means of estimating the amount of ammonia gradually produced. In all cases, therefore, where the action of ammonia is not desired, an acid gelatine should be used, as well as when the emulsion is to be boiled. When ammonia is actually wanted, it is better to add it directly to the emulsion, and then it will be possible to check the length and intensity of its action.

V.—INFLUENCE OF THE PRODUCTS OF DECOMPOSITION OF GELATINE ON THE SENSITIVENESS OF AN EMULSION.

The sensitiveness of a gelatine emulsion is increased not only by long-continued heating, by which the gelatine is partially decomposed, but also by boiling for not more than a quarter of an hour, when no alteration of the gelatine can be observed. Still more powerful is the fact that an emulsion of gum-arabic will also be made more sensitive both by long-continued digestion at a moderate temperature, as well as by boiling a short time. Now, gum-arabic does not alter in boiling; we may conclude, therefore, that, in all these cases, the increased sensitiveness is due to a change in the physical condition of the silver bromide. Many samples of gelatine contain substances of unknown composition, which, in the presence of ammonia, reduce bromide of silver, and give rise to a foggy emulsion. Such samples of gelatine should be avoided.

Another factor in the attainment of increased sensitiveness may possibly be, as pointed out by Dr. Lohse, the degree of porosity of the gelatine film. Substances which, like alum, have a tanning action, make the film leathery and impervious, and a less sensitive plate is the consequence. Under ordinary circumstances, however, I do not think this difference is sufficiently great to be observable in practice. At any rate, I have not remarked any considerable difference in this respect between a hard collotype gelatine and a soft and fine sample, though the comparative toughness of the two was just as marked after they had been treated in the usual way with ammonia.

VI.—CHOICE OF A GELATINE FOR EMULSION.

As the result of the experiments that I have made on this subject, I recommend the following points, to which attention should be directed in choosing a gelatine for emulsion purposes.

1. When ammonia is not to be used, the gelatine should have an acid reaction; when ammonia is used, it is a matter of indifference. The opinion has been repeatedly expressed in English journals,[1] that the clear descriptions of gelatine are invariably acid. This is only true in a certain way. All alkaline gelatines that I have come across were cloudy; but all acid samples were not clear and transparent.

2. A test of the emulsion at a temperature of 40° C. can be made by means of silver bromide and ammonia.

Ammonia as recommended below should not be added before, but after digestion, and just before the washing stage. A plate may be coated with the unwashed emulsion, and, after being allowed to set, may be soaked in water for twelve hours. When dry it should be treated with a normal developer, and give clear glass. If any fogginess is apparent we may conclude that the gelatine employed contains injurious by-products, and it should be rejected.

3. Ordinary collotype gelatine may be taken, but that sort is to be preferred which gives the clearest and hardest jelly, and absorbs little water.

4. The gelatine must be free from fat, otherwise there will be depressions in the film, and bright spots with blurred outlines in the negative. A gelatine of this kind is, however, often employed when the emulsion is prepared with the addition of ammonia. In this case the fatty matter is probably saponified, and the spots will disappear.

5. A 4 per cent. solution of gelatine sets thoroughly at a temperature of about 20° C. Since this corresponds to a melting point of about 28° C. or 30° C., it is now an easy matter to determine roughly the melting points of various sorts of gelatine, and to infer that the setting points will be some 8° or 10° lower. The higher the melting and setting points are, the

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[1] *Photographic News*, 1880, xxiv., 282, 307.

better is the gelatine, so long as it dissolves completely in water of a temperature of 40° C. or 50° C.

VII.—FRILLING AND EXPANSION OF THE FILM

Gelatine films on glass have occasionally a very awkward way of expanding when heated with water, especially when the water contains salts in solution. In this case they are liable, as I have said, to expand considerably, and to form frills and blisters. As the cause of this phenomenon does not appear to be accurately known, I give the result of some of my own observations, which may throw some light on the subject. Frilling and expansion of the film are promoted:—1. By coating the plates thickly; 2. When the gelatine absorbs a good deal of water; 3. When the emulsion has been digested a long time over heat; 4. When the gelatine contains gum-arabic.

The first of these faults can be cured by coating the plates more thinly; the second by addition of alum or chrome alum, or by soaking the plate before development in a cold saturated solution of alum. The latter is generally efficacious, if the plate be developed immediately after coming out of the alum bath. If this fails, the plate may be rinsed and dried, and then developed. By this means the absorptive power of gelatine is a good deal diminished.

It is remarkable that an otherwise excellent gelatine will often possess this fault when it contains a gum like gum-arabic, soluble in water, or even some gummy substance like gelatine, which has been altered by long-continued heating. Possibly there may be a change in the diffusive relations, and a gelatine will be more especially liable to expansion and frilling when a developing solution containing salts is removed by washing.

CHAPTER IV.

SOLARIZATION: ITS CAUSES AND APPLICATION

MOSER was the first to study this phenomenon, and Captain Abney has recently devoted a considerable amount of attention to the subject, with very valuable results.

Solarization is the effect produced in a plate which has been exposed for a considerable time, and is made evident by the development being irregular either all over the plate, or in individual parts. The primary effect of over-exposure is to cause fog on development, but if the exposure be carried still further, an opposite result supervenes; the original impression disappears, and the film loses more or less its tendency to fog under the action of the developer. No solarization is apparent in a plate exposed for a short time. The more generally insensitive the film is, the longer does it require to produce the effect of solarization. To obtain a more or less complete effect of solarisation requires some hundreds, or even a thousand times, the exposure necessary to produce a negative.

Abney gives, as an explanation of this phenomenon, that the oxygen of the air combines with the altered bromide or iodide of silver, the compound so formed being little if at all acted upon by the developer.

The best proof of this is offered by his experiment, in which iodide or bromide of silver exposed to light in presence of hydrogen or other substances, such as gallic acid, which absorb oxygen, do not show any effect of solarisation. On the other hand, plates exposed in substances which readily part with oxygen, such as bichromate of potash, oxide of hydrogen, or ozone, become solarized in the usual way.

Wet bromo-iodide collodion plates, exposed under a film of silver nitrate, are rapidly solarized, but if tannin or gum-gallic plates be employed, this effect rarely ensues.[1]

Iodide of silver appears to solarize rapidly under the action of the blue rays. In the case of bromide and bromo-iodide of silver, the red and ultra-red rays have the oxidising action, and since these are of little photographic value, the operation takes longer than in the case of iodide of silver plates. The effect is much more apparent in the case of gelatine plates than in the case of collodion plates with a preservative, owing, probably, to their greater sensitiveness to light. Bromide of silver gelatine solarizes quicker than bromo-iodide, a matter of importance in landscape work.

There is no doubt that under ordinary circumstances, a gelatino-bromide plate may become powerfully solarized before any trace of discolouration of the film is apparent, but the characteristic loss of developing power renders the spots which have been solarized visible, although discolourization may be barely recognized.

If an emulsion plate be exposed beforehand to weak diffused light, it will solarize more rapidly than if it had not been so exposed. In one case a plate which had been so exposed showed this effect after an exposure to lamp-light of ten seconds.

Although this phenomenon is usually much dreaded by photographers, its principle has within recent times been applied to the assistance of photography.

If a gelatine plate be exposed under a positive, sufficient intensity can be obtained in one or two seconds. If the exposure

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[1] *Photo. News*, 1880, xxiv., 78.

be prolonged to thirty or forty-five seconds, we shall obtain a negative in which the highest lights are positive. A still longer exposure, lasting over three to five minutes, results in a reversal of the image throughout the whole plate, and, if carried yet further, the image loses definition and begins to fade away.

Janssen, in his studies on solar photography, observed that an exposure to light of from $\frac{1}{2}$ to 1 second (the correct exposure being $\frac{1}{200000}$ of a second) produced a reversal of the photographic image by the action of solarization. The result of a still longer exposure was to cause a second reversal of the image, and after exposure a million times longer than was necessary to produce a negative in the ordinary way, one of the second order resulted, the image fading away after further exposure. ~~Herack~~ Haack alluded to the subject at the May meeting of the Photographic Society of Vienna (1880), and expressed an opinion that the principle might be made available for multiplying negatives.

Bolas' method of utilizing the principle of solarization will be found described in the *Photographic News*, 1880, p. 304. A gelatino-bromide plate is soaked for a few minutes in a 4 per cent. solution of bichromate of potash, and after this it is rinsed for a few minutes in a bath composed of equal volumes of alcohol and water. On removal from the alcohol bath it is laid down on its back, and the superfluous moisture removed from the film with blotting-paper, after which it is placed in a warm place to dry. When dry, it is exposed under a negative, and about the same exposure given as would be necessary for printing in carbon from the same negative; that is, from two to five minutes in sunshine, or from ten to fifteen minutes in good diffused light. After exposure, the plate will be impressed with a delicate and perfect positive, owing to the darkening action on the bromide of silver, as well as on the bichromate of potash.

The plate is then soaked in cold water to remove the excess of bichromate of potash, and, after that, developed in either pyrogallic acid or ferrous oxalate ; but, on the whole, the former is to be recommended for the purpose.[1]

Under the action of the developer the picture rapidly makes its appearance, and, after fixing, gives an intense negative. If the exposure has been too short, the developement is rapid, and the picture flat ; over-exposure gives a hard picture, which takes a long time to develop.

In conclusion, I may state that the effect of solarization may often be traced as much to the action of the developer as to that of light. The tendency to this effect will be most apparent when a strong developer without sufficient restraining bromide is employed, or when the development is continued for a long time.

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[1] My view is, that the combination of gelatine and chromate becomes insoluble in light, and development is thereby hindered.

CHAPTER V.

FADING OF THE LATENT IMAGE.

If a considerable time elapse between the exposure and development of a photographic plate, the actinic impression loses strength, and the image, on development, is neither so brilliant nor full of detail as when developed immediately after exposure.

The subject has been studied in connection with various forms of iodide of silver plates combined with physical development by Reissig, Carey Lea, and others.

Reissig was the first to point out that pure ~~bromide~~ iodide of silver, prepared on a silvered plate with iodine or iodide of potassium containing no excess of silver nitrate, soon loses in a dry state the latent image; while, on the other hand, iodide of silver containing an excess of silver nitrate and suspended in collodion will, after washing, or when preserved in a solution of silver nitrate, retain the actinic impression for an unlimited time. Draper has proved that Daguerreotype plates lose their image when kept in the dark.

The degree in which the fading takes place evidently depends on the method by which the plates are prepared. In the case of dry plates, the evidence is very strong. Carey Lea, in experimenting with tannin plates prepared according to Russel's formula, and containing an excess of silver nitrate, found that although no signs of deterioration were apparent after a month's keeping, yet after that time the image got feebler and feebler, and at the end of six months there was hardly any trace of the picture left. Vidal recommends that tannin plates which are to be kept from seventeen to twenty days should be exposed from seven to ten times as long as would be necessary if developed at once.

England states that bromo-iodide collodion plates sensitised in a bath and treated with albumen, keep well after exposure. Gum-gallic plates also keep well, and may be successfully developed six months after exposure.

Carey Lea points out that collodio-bromide plates prepared with excess of silver, and treated with a litmus preservative, soon lose any latent impression; but if a solution of cochineal be employed, the plates, so far as this defect is concerned, are improved.

In the case of collodio-bromide prepared with excess of silver, Warnerke and Jennings found that the image disappears so quickly, that in fourteen days after exposure nothing but the sky appeared in development. Gelatine emulsion plates prepared with excess of soluble bromide retain the latent image for a long time.[1]

The reason of this fading may be due to some of the following causes :—

1. Oxidation may take place. Reynolds was the first to point out that ozone destroys the latent image, and he suggested that possibly the change produced in plates after exposure might be due to the same cause. This may be true in some cases, but not always, as the effect is apparent quite as much in plates treated

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[1] Blow's theory that the image on a gelatine plate increases in vigour between exposure and development is very doubtful. In reference to this subject I may recal Laoureux's statement that an exposed gelatine plate, if pressed in contact with another unexposed plate, communicates the latent image in such a manner that a second picture of equal intensity can be developed on the unexposed plate.

with an albumen preservative, which has no attraction for oxygen, as in tannin plates, where a body which absorbs oxygen is present; and besides, it does not account for the wonderful keeping qualities of gelatine plates after exposure.

2. The presence of nitric acid generally destroys the latent image. Abney mentions a case in which a collodio-bromide film decomposed spontaneously, owing to the pyroxyline developing nitrous acid,[1] the natural consequence being a destruction of the image. Any danger of this sort can easily be guarded against by the employment of an alkaline preservative.

3. Iodide of silver prepared with excess of silver nitrate is decomposed by light, and the following reaction is generally accepted as indicative of the action that takes place:—

$$12AgI + 6AgNo_3 + 3H_2O = 6Ag_2I + 5AgI + 6HNO_3.$$

Silver iodide, silver nitrate, and water give sub-iodide of silver, iodide and iodate of silver, and nitric acid.

The reaction is the same in the case of bromide of silver. Free nitric acid cannot have much effect in small quantities, otherwise iodide of silver plates prepared in the bath would not retain the image so long as they are known to do.

If we examine the following equation, we can understand the reason why dry plates prepared with excess of silver nitrate keep badly after exposure:—

$$4Ag_2Br + 6HNO_3 = 4AgBr + 4AgNO_3 + N_2O_3 + 3H_2O.$$

represents a gradual change during which nitric acid destroys the image, and sets free nitrous acid, which also assists in the same action. This fact will account for the bad keeping qualities of tannin plates after exposure, since the nitrous acid liberated will not combine with tannin; while in the case of

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[1] The spontaneous decomposition of pyroxyline is very liable to occur if much nitric acid has been added to the emulsion, with the view of preventing fog.

albumen plates, which are superior in keeping qualities, no nitrous acid is set free.

In connection with the formation of the latent image in the presence of various other sensitizers, Vogel has pointed out that the character of the latent image formed on iodide of silver in presence of potassium ferrocyanide is very different to that formed in presence of sodic sulphite. In the latter case, no free acid is liberated, and no iodate of silver formed, and the image formed is much more permanent than that formed in presence of potassium ferrocyanide.

If a strong dose of nitric acid or aqua-regia be added to a collodion emulsion, a proceeding often resorted to for the purpose of restraining fog, the latent image is rapidly destroyed.

The power that gelatine plates possess of retaining for a long time unimpaired the latent image, appears to me due to the fact that, owing to the absence of an excess of silver nitrate, the bromine liberated during exposure combines with the gelatine, which thus acts as a sensitizer, without at the same time setting free an injurious oxidising acid such as nitric acid.

IV. The fading of the image may be due to the fact that the bromine or iodine liberated during exposure combines with the sensitizer, and after the plates have been kept for some time, the sub-bromide or sub-iodide becomes reconverted into bromide or iodide by absorption of bromine or iodine, a process in which the oxygen of the atmosphere would assist.

This reaction would not be likely to occur in the case of bromide or iodide of silver prepared with excess of silver nitrate. If exposed in the presence of sodic sulphite, or potassium nitrate, a reaction of this nature would occur—

$$12AgI + 3Na_2SO_3 + 3H_2O = 6Ag_2I + 6HI + 3Na_2SO_4$$

the hydriodic acid so formed gradually destroys the latent image.

Bromide of silver, under these circumstances, would not be much affected. Hydrobromic acid is, no doubt, given off, but it takes much longer to attack the image than hydriodic acid.[1]

V. In conclusion, the oxidising action of the atmosphere may be alluded to as probably, under these circumstances, causing a partial destruction of the image. Sulphuric acid and coal gas also prevent the development of a picture, by causing a partial reduction of silver.

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[1] Should hydrobromic acid be formed in the gelatine film upon exposure to light, it would scarcely be in a free state, since dilute organic acids are present. In the form of a salt, the separated bromine would be with little, if any, effect upon the latent image

CHAPTER VI.

DEVELOPMENT OF BROMIDE OF SILVER PLATES.

I.—DEVELOPMENT WITH FERROUS SALTS.

IN 1877 Carey Lea suggested the possibility of developing plates containing bromide of silver with ferrous salts. He alluded to various possible forms of developers, such as ferrous lactate, salycilicate, succinate, citrate, &c., and especially mentioned ferrous oxalate.

Potassic ferrous oxalate compares very favourably as a developer with pyrogallic acid, and is far superior in its reducing action to any other compounds in connection with ferrous oxalate.

In a paper presented to the Imperial Academy of Vienna, in January, 1880, I described the reducing action of this body on the metallic salts, and especially on the haloid salts of silver. The latter, when treated with warm solutions of ferrous oxalate after exposure to light, are at once reduced to a metallic state.

As a developer, ferrous oxalate had not been employed in Germany or Austria, owing to the complicated character of the preparation. I have devoted some time to its study, and may say that the simplifications I have introduced into its preparation have caused its general adoption. The method of preparing the developer by boiling 100 c.c. of a 20 per cent. solution of neutral potassic oxalate with from 6 to 10 grammes of ferrous oxalate is inconvenient and tedious. The method, which I was the first to propose, consists simply in mixing together 3 parts of a 25 per cent. solution of neutral potassium oxalate with 1 part of a 25 per cent. solution of ferrous sulphate.[1] A deep red solution results, which will be muddy if too much of the iron solution has been added. Slow plates, developed with ferrous oxalate, do not require any addition of bromide of potassium, but rapid plates will fog, unless an addition of about two to ten drops of a 1-10 solution is made to every 100 c.c. of solution. Complaints are constantly made that it is difficult to develop an under-exposed plate; in other words, that it is necessary to accommodate the exposure to the developer, instead of *vice versa*. A question which reached me from Mr. Forrest, of Pontypridd, through the *Photographic News*, led me to the following method of controlling the development. The potassic oxalate and ferrous sulphate, in the proportions given above, are measured out, but not mixed, a few drops only of the latter being added to the potassic oxalate immediately before development. A very much over-exposed plate will develop rapidly. If the image is thin and weak, more intensity can be gained by adding a few drops of a 1-10 solution of potassium bromide, and a little more ferrous sulphate. Generally speaking, 0·1 per cent. bromide of potassium will be found sufficient to restrain the action without making the development too long. If the potassic oxalate be acid, it requires less of the restrainer than when in a neutral condition. The shorter the exposure, the more ferrous sulphate is required. A normal exposure requires the whole addition of ferrous sulphate, but the latter should never exceed one-third of the potassic oxalate solution, otherwise the developer will be cloudy.

Ferrous oxalate proves of great value in out-door photography, in which, as a rule, plates are over-exposed. I certainly recommend in all cases a full exposure, as, by the means indicated

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[1] The simplest plan is to take cold saturated solutions of ferrous sulphate and potassium oxalate, and mix three volumes of the latter with one of the former.

above, there is no difficulty in producing a good negative out of a plate which has been exposed four or five times too long. Under-exposed plates will never make a good negative with any form of developer.

A very strong concentrated solution can be prepared—which may be termed a reserve developer—by digesting a supersaturated solution of potassic oxalate with ferrous oxalate. In this way, a large quantity of potassic ferrous oxalate can be brought into solution without precipitating when the solution cools. Fifty or sixty grammes of potassic oxalate are dissolved in 100 cubic centimetres of water by heat, and 17 to 20 grammes of ferrous sulphate added. The iron dissolves at once; much more readily, in fact, than a corresponding amount of potassic oxalate. When the salts are dissolved, the solution is put into a well-corked bottle, and allowed to stand for twenty-four hours in a cool place. When cold, crystals of potassium sulphate will deposit, but none of the effective oxalate. The concentrated solution now contains about 12 per cent., or about double as much ferrous oxalate as the normal mixture, and its developing action will be found to be considerably increased. The solution may now be placed into small bottles, in which form it will keep for a long time. After standing for a long time, orange crystals of potassic ferrous sulphate separate out.

If the picture is not sufficiently vigorous after five minutes' development under the normal mixture, the latter may be poured off, and the reserve developer, with the addition of a small quantity of potassium bromide, substituted. It is not easy to work with the reserve developer when the plate has been under-exposed.

Other experimenters have suggested the addition of foreign substances to the ferrous-oxalate developer. Warnerke suggested at the Photographic Society of Great Britain the use of citric acid as a restrainer. The latter acts in much the same way as oxalic or acetic in removing any chance of an alkaline reaction. Wilde has recommended the use of gelatine or glycerine; Brooks advises collocine and lump sugar. I find, generally, that such additions tend to give hard negatives. For developing portraits, a few drops of hyposulphite solution (1 hyposulphite, 200 water) may be added with advantage.

It may be asked why we always employ potassium oxalate, in preference to the sodium or ammonia salts. A glance at the following rates of solubility will show that the potassium salt will give a much more concentrated developer than either of the others. While 1 part potassium oxalate dissolves in 3 parts cold water, the ammonia salt requires 24, and the soda salt 32 parts. On the other hand, the ammonia salt dissolves readily in boiling water, and a saturated solution of this salt takes up as much ferrous oxalate as a solution of potassium oxalate.

(*a.*) If ferrous oxalate be boiled with a 1 per cent. solution of ammonia oxalate, it retains, on cooling, about the same as the potassium salt, *i.e.*, 0·14 per cent. of ferrous oxalate.

(*b.*) A 20 per cent. solution of ammonia oxalate takes up 4·90 per cent. of ferrous oxalate. Potassium oxalate takes up 6·76 per cent.

(*c.*) A 30 per cent. solution does not take up more than a 20 per cent. solution.

Under no circumstances will a solution of ammonia oxalate take up as much ferrous oxalate as potassium-oxalate solution, although when the former is boiling it will dissolve double as much ferrous oxalate as it will when cold. I may add that a 40 per cent. solution of potassic oxalate takes up, when boiling, 12·62 per cent. ferrous oxalate, and retains 9·4 per cent. in solution when cold.

The sodium oxalate has a still smaller dissolving power. A 10 per cent. solution of this salt only takes up at 100° C., 12.18 per cent. ferrous oxalate, and retains, on cooling, 0·89 per cent.

A 20 per cent. solution of ammonia oxalate can be readily employed in the preparation of a ferrous-oxalate developer, and will be found even more effective than a corresponding potassium-oxalate solution; but as the degree of concentration of the latter can be considerably increased, and the former is not capable of being so, the advantage evidently remains with the potassium salt.

The reducing agent in the ferrous oxalate developer is stated by Valenta to be potassic ferrous oxalate, having the composition Fe $(C_2O_4)_2K_2 + H_2O$. This salt collects in small transparent orange crystals, which in a moist state greedily absorb oxygen, but when dry, remain tolerably unaffected by the atmosphere. Treated with water, a partial disintregation takes place, and the insoluble yellow ferrous oxalate separates out; but in presence of an excess of potassic oxalate the solution is complete. If the developer be in a very concentrated form, ferrous oxalate is apt to be precipitated.

The ammonium ferrous oxalate salt has the composition Fe $(C_2O_4)_2(NH_4)_2 + 3\ H_2O$. It behaves in a similar manner to the potassium salt, but is more difficult to prepare, and less stable.

The sodium salt I have never been able to prepare.

The ferrous oxalate developer absorbs oxygen from the atmosphere when in a neutral condition, and an orange brown salt, consisting of basic ferric oxalate, separates out; the remaining solution turns green, and contains the double ferrous oxide and potassium ferric oxalate, which, owing to its inferior solubilities, forms into emerald green crystals.

C.—Development with Other Salts of Iron.

A short time ago (1880), Carey Lea stated that in addition to ferrous oxalate, there were organic salts of ferrous oxide which possessed a reducing power on bromide of silver. Metaphosphate, hyposulphate, hydrosulphite, metapectate, and ferrous ammonium chloride have all an effect more or less, but he recommended the phosphate, borate, and sulphite specially, and as these salts are insoluble in water, it was necessary to dissolve them in either the oxalates or tartrates of the alkaline metals. He communicates further particulars on the subject of these developers.

1. *Ferro-Boro Developer.*—Carey Lea states that with this, as well as the sulphite developer, he attained the best results, and he prefers it to ferrous oxalate:—

Borax	100	grains
Neutral potassic oxalate	400	„
Ferrous sulphate	120	„

These are boiled together in 6 ounces of water, and after standing for eight hours, the solution is filtered; according to Carey Lea's practice, it is diluted with 3 to 4 parts of water, and requires the use of potassium bromide to restrain its excessive energy. Other experimenters find that in the dilute form employed by Carey Lea it has very little developing power, and in a concentrated form it is not more energetic than an equally concentrated ferrous oxalate solution.

A very useful effect can be obtained by adding a proportion of a saturated solution of borax to the ordinary mixture of potassic oxalate and ferrous sulphate. The addition will only be of benefit if the ferrous oxalate solution is slightly acid, and may be made up to 20 per cent. Borax brings out detail and increases the energy of the developer, by producing a slightly alkaline reaction, without at the same time giving the same tendency to fog as is the case with potassic carbonate. But at the same time, it will be found necessary to increase the amount of potassium bromide in proportion to the increase of borax. The use of borax gives density, and if much potassium bromide be employed, the resulting negatives are liable to be hard.

If the ferrous oxalate solution be absolutely neutral, no advantage is to be gained by addition of borax. The only effect it appears to have is to impart a weak brown tone to the resulting negative.

2. *Ferro-Phosphate Developer.*—Ferrous phosphate may be prepared in the following manner:—200 grains of neutral ammonic oxalate are dissolved with 50 grains of sodic phosphate in 4 ounces of warm water, and 75 grains ferrous sulphate added. Ferrous phosphate will dissolve as readily in ammonic-oxalate as in potassic oxalate. In practice dilute with 3 or 4 parts of water, and add a few drops of a solution of potassium bromide.

I find the developer gets very thick by keeping, and does not develop so actively as the borate developer.

Ferro-Sulphite or Oxalo-Sulphite Developer.—Carey Lea describes this developer as second only to the borate in energy.

1.—Neutral potassic oxalate	... ...	440 grains
Neutral sodic sulphite	... ...	60 ,,
2.—Ferrous sulphate	... ...	160 ,,

The potassic oxalate and sodic sulphite are dissolved in six ounces of warm water, and the ferrous sulphate added. After solution is complete, the mixture may stand for six to eight hours, and be then filtered. According to Carey Lea, this developer is as active as the borate, and gives the same deep colour and easy intensity, but requires more restraining than the ordinary oxalate. In my experience no benefit worth mentioning is to be obtained by this addition of sodic sulphite.

4. Hypophosphoric acid, saturated with iron filings, yields a salt that possesses no developing power, but warm solution of sodic hyposulphite and ferrous sulphate mixed together have a powerful developing action. The same solutions mixed cold fail to exhibit any developing power, but if brought to boiling point they acquire the power and retain it after cooling.

This developer is quite free from any tendency to fog, but requires a long exposure, and gives no detail in the shadows.

Ferro-Antimonic Tartrate.—A mixture of ferrous sulphate and tartar emetic remains clean, and develops a picture of a beautiful golden brown colour. It is not equal in energy to others here mentioned.

5. *Ferrous-Tartrates.*—Alkaline tartrates can be substituted for the oxalates in most of the cases referred to. The potash salt is not very suitable, because of its readiness to form the very sparingly soluble bitartrate. The neutral sodium and ammonium salts, or Rochelle salt (potassic sodic tartrate), can be employed.

The ferrous-boro-tartrate developer is more energetic than the ferro-tartrate modification, probably from the fact that it contains no free acid. It may be prepared as follows:—

Neutral ammonium tartrate	200 grains
Borax	50 ,,

are dissolved in three ounces of water. When fully dissolved, add 50 grains ferrous sulphate, and allow the solution to stand for six or eight hours, after which filter. The addition of potassium bromide will be necessary during development. The energy of this mixture is, according to Carey Lea, equal to that of the oxalo-boro-tartrate already described, but there is a want of contrast in the resulting picture.

I find that the solution prepared as above possesses so little energy as to require more than ten times the exposure necessary with the ordinary ferrous-oxalate developer. It is interesting however, that there are other ferrous salts possessing developing power, and that the tartrates are similar in their action to the oxalates.

The effect of different developers on the colour and character of the image is often very curious. If iodide of silver be present in the emulsion, the image, when developed with ferrous-oxalate, is an olive black; when developed with ferrous phosphate dissolved in ammonia tartrate, it is brick red. If a mixture of ferrous sulphate and neutral sodic tartrate be employed without potassium bromide, a brownish red coloured picture results; if bromide be used, the colour is olive black.

II.—Development with Pyrogallic Acid.

The changes which the composition of alkaline pyrogallic acid has undergone since its introduction by Russell in 1862 are numerous.[1] The latter employed ammonia as the alkaline component, and observed that if too much of it be added in the development of dry plates sensitized in the bath, fog made its appearance. The extraordinary restraining power of potassium bromide was not then known, and in my experience fog is more liable to make its appearance in the case of bromide plates sensitized in the bath and containing a trace of free silver, than in emulsion plates in which there is no such excess. This, probably, is the reason why, in earlier days, weak pyrogallic developers were employed in the development of dry bath plates; while with the advent of bromide emulsions, which, as a rule, contain no excess of free silver, strong developers became popular. In 1863, Sutton suggested the employment of potassium carbonate instead of ammonia, on account of its freedom from fog and stains. In the second edition of his work on the preparation of tannin plates, Russell recommended dilute ammonia carbonate, and the addition of an alkaline solution of potassium bromide. Other substances have been suggested instead of ammonia, such as the bi-carbonate of potash, soda, lime syrup, sodic metaphosphate, &c.

The degree of concentration of the alkaline developer is of the utmost importance. A concentrated developer not only admits of a shorter exposure, but brings out the image more rapidly, and with a greater amount of detail. The dilute solution (1 to 200) of ammonia carbonate, which was in use ten to fifteen years ago, requires five times as much exposure as the 1 to 5 solution recommended by Wortley. The latter, who was the first to urge the employment of concentrated developers, insists that it

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[1] *Br. Journ.*, November 5th, 1862.

was impossible to obtain the same sensitiveness with weak as with concentrated developers. The value of the alkaline developer depends as much on the nature of the alkali employed, as on the degree of concentration of its elements. It is well known that ammonia is much more energetic than sodic carbonate, and this fact must be taken account of in preparing the developer.

In taking up this subject, Capt. Toth and myself prepared 15 per cent. aqueous solutions of potassium bicarbonate, anhydrous sodic carbonate, ammonic sesquicarbonate, and 10 per cent. solutions of ammonia and potassic hydrate. To every 20 to 30 c.c. of the first three solutions, 5 c.c. of a 5 per cent. solution of pyrogallic acid were added, and 10 to 15 drops of a 1-10 solution of potassium bromide. To every 100 c.c. of water, from 2 to 5 drops of the ammonia and potassic hydrate were gradually added, and pyrogallic acid and potassium bromide in the same proportions as before. The experiments were made with collodion emulsion,[1] in which the action of the various alkalies employed is the same as in gelatine emulsions. In photographing a plaster cast made up with dark drapery, the solution of potassium and sodic bicarbonate gave only the highest lights, while ammonia developed a thoroughly well-exposed negative. The formula given by Obernetter and Haack for an alkaline developer[2] is more energetic with ammonia to the extent of 10 drops to every 250 c.c. of water than with a saturated solution of ammonic carbonate, used in the proportion of 1 to 3, and the latter in its turn proved more powerful than the sodic bicarbonate. Equal proportions of concentrated soda and ammonic sesquicarbonate proved

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[1] Prepared principally with a small excess of silver, which was afterwards removed with calcic chloride. Plates prepared with excess of bromide, and treated with a tannin preservative, were also employed.

[2]

Pyrogallic acid solution (1-10)	5 c.c.
Bromide of potassium (1-10)	4 c.c.
Water	250 c.c.
Ammonia	10 drops.

approximately the same. The use of soda is distinguished by the clear and brilliant negatives which result, and in this respect is superior to ammonia, and even to the ammonic sesquicarbonate. A cold saturated solution of the former[1] gives a developer which I prefer to any other form for collodion emulsions.

The action of a ferrous oxalate developer containing 6 per cent. of ferrous oxalate may be classed as intermediate to that of a pyro developer containing ammonia, and another containing ammonic carbonate, although it is considerably close to the former. If the developer contains 10 per cent. ferrous oxalate, it is superior to Obernetter's formula, and, when properly controlled with potassium bromide, gives clear, soft negatives full of detail. The action of potassic hydrate is very slow, and it readily gives fog. With the exception of the carbonate or sesquicarbonate of ammonium, any alkali used in excess will give chemical fog, especially when the plates employed have been prepared with excess of soluble bromide.

If carbonic oxide be passed through a solution of ammonic carbonate, such as is usually purchased in shops, it passes into the bi-carbonate. The dry salt does the same by absorption of moisture from the atmosphere. In either case its value as a photographic agent is very much reduced. Carey Lee has pointed out the inferiority of potassic bi-carbonate as compared with ammonic carbonate, and we may conclude that the bi-carbonates have generally little photographic value.

The following experiment is instructive. A pyrogallic developer containing 5 per cent. ammonia and a certain amount of potassium bromide will be very energetic, and probably give fog;

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[1] The following formula can be recommended:—50 c.c. of a cold saturated solution of calcined soda is mixed with 5 c.c. of an (1-10) alcoholic solution of pyrogallic acid, and 20 drops of a (1-10) solution of potassium bromide added. The water is not so necessary as when ammonic carbonate is employed.

but if the pyrogallic acid and bromide be dissolved in a saturated solution of ammonic carbonate, as much as ten times the amount of ammonia previously added may be employed without danger of fog. In the second case, hydric ammonic carbonate is formed, which is less energetic than ammonia, but more so than the carbonate; consequently the effect of the latter can be improved by the addition of ammonia. The possible alkaline components are here tabulated in their inverse order of merit:

1. Bi-carbonate of potash or soda.
2. Bi-carbonate of ammonium.
3.
   - Carbonate soda.
   - Sesqui-carbonate ammonia.
4. Carbonate ammonium.
5. Potassic ferrous oxalate.
6.
   - Oxalate.
   - Hyposulphite.
   - Ammonia.
7. Potassic hydrate.

In order to employ these substances to their best advantage, it is necessary to use bromide of potassium. Of the substances mentioned above, ammonia and potassic hydrate are exceedingly energetic, and require to be used in a very dilute form. Shortness of exposure can be compensated for by increasing the concentration of the alkaline elements when we are employing alkaline carbonate in conjunction with pyrogallic acid, or the strength of the ferrous oxalate solution, such concentration being, of course, only limited by the solubility of the salts. The alkaline developer can be made to act much more energetically than ferrous oxalate by addition of ammonia; but in proportion to this addition is the danger of fog. If we work so as to keep clear of fog, we shall find that the alkaline pyrogallic developer really requires a longer exposure than ferrous oxalate. The latter, if properly restrained, gives no tendency to fog, and, since its strength may be increased very considerably, it follows that we can reduce the necessary exposure proportionately.

In regard to alkaline pyrogallic development, it may be stated absolutely that increase of amount of ammonia shortens exposure; but an increase in concentration of the latter is highly conducive to fog.

IV.—THE CORRECT TREATMENT OF THE PYROGALLIC DEVELOPER.

Although the use of alkaline pyrogallic as a developer has been known for a long time, and a good deal has been written on the subject of its rational use, it is advisable to return to the matter, because a thorough knowledge of its capabilities is of extreme importance. As an example of a powerful and simple developer, I take Obernetter's formula—

Alcoholic solution of pyrogallic acid	1 to 10	5 c.c.
Potassium bromide	1 to 10	4 c.c.
Water		250 c.c.
Ammonia		10 drops

An increase of ammonia causes rapid development, as well as a slight increase of sensitiveness, but is conducive to fog. Potassium bromide keeps the shadows clear, and heightens the contrast. An increase in the amount of pyrogallic acid has not much effect, and we can, in the above formula, make a difference of one or two cubic centimetres in the amount of the former without sensibly affecting the result.

The action on the character of the image by simple dilution of the developer is not so familiar. Dr. Heid, who has recently made a series of experiments on development of gelatine negatives, states that every gradation of contrast is possible by simply diluting the developer. For the production of very soft harmonious negatives he recommends the following:—

Pyrogallic acid solution	1 to 10	3 c.c.
Potassium bromide	1 to 10	1 c.c.
Water		500 c.c.
Ammonia		15 to 20 drops

Swan's experiments on the same subject may be quoted. He exposed his gelatine plates for the same length of time, and developed them in different ways. The pyrogallic was used of different strengths for three of the plates, the proportions being 1 in 120, 1 in 240, 1 in 480.

The same quantity of the following ammonia and potassium bromide solutions was added to each of the solutions:—

Potassium bromide	2 parts
Ammonia	3 ,,
Water	240 ,,

The density of the resulting negatives when developed for some time was in proportion to the strength of the pyrogallic solution. A long development with the dilute solution gave the same effect as a shorter development with the more concentrated solution.

In a second series of experiments the strength of the pyrogallic solution was constant, while the proportions of ammonia and bromide were varied. Corrections in the exposure can be made by varying the amounts of ammonia and bromide. Swan demonstrated this by doubling the amount of bromide and ammonia in the case of a plate which had only received half the correct exposure, the resulting negative being equal to one correctly exposed. Another which had had three times the correct exposure was successfully developed by adding a small quantity of extra bromide to the normal developer. A simple dilution of the developer would have also been effectual.

Edwards' glycerine developer has been warmly taken up, and its merits are highly spoken of.[1] It allows a greater range of exposure, with an easy control over the density of the picture, and gives more brilliancy than the simple pyrogallic developer.

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[1] *Photographic News*, 1880, xxiv., 177.

The glycerine, too, improves the keeping power of the pyrogallic solution:—

A—Pyrogallic acid	1 ounce
Glycerine	1 ,,
Methylated alcohol	6 ,,
B—Potassium bromide	60 grains
Glycerine	1 ounce
Ammonia (·880)	1 ,,
Water...	6 ounces

These solutions will keep for a long time. In development, equal quantities of the A and B solutions are employed, diluted with water 1 in 15. If the development be correct the picture makes its appearance rapidly, and is fully developed in about a minute. The operation should not be hurried, but the plate left in the dish till the details are well out, and the necessary intensity obtained. Under-exposed plates require more ammonia. If the image comes out very rapidly owing to over-exposure, the developer is thrown off, and the plate flooded with the pyrogallic solution diluted as before. This will be found sufficient with what remains in the dish of the ammonia to complete the development.

Henderson's ferrocyanide developer is a favourite with some photographers, while others complain of a tendency to fog.[1] To 60 c.c. of a nearly concentrated solution of potassium ferrocyanide (Fry recommends 30 c.c. saturated solution of potassium ferrocyanide to 30 c.c. of water)[2] 2 c.c. of a 1-10 pyrogallic solution is added, and two to four drops of ammonia. Vogel finds that this developer gives more density as well as detail with some forms of gelatino-bromide plates, while with others there is a tendency to fog.

Nelson recommends a pyrogallic developer[3] containing an addi-

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[1] *Br. Journ.*, 1879, xxvi., 861.
[2] *Photo. News*, 1880, xxiv., 895.
[3] *Photo. News*, 1880, xxiv., 227.

tion of 5 to 10 per cent. white sugar. Sugar here takes the place of the glycerine in Edwards' developer, but probably it has more of a physical than a chemical effect.

Hydrokinone—Pyrocatchin, and Phloroglucin.

Capt. Abney has suggested quite recently a new organic developer consisting of hydrokinone, a derivative of chinone, and soluble either in water or alcohol.[1] An aqueous solution decomposes rapidly, but an alcoholic solution will, like an analogous preparation of pyrogallic acid, keep for months. A plate developed with a 2 per cent. aqueous solution of hydrokinone, to which a few drops of ammonia have been added, is thin, but admits of silver intensification. A 4 or 6 per cent. solution gives plenty of density. According to Capt. Abney, this developer is free from any tendency to fog, and only requires about half the exposure necessary with alkaline pyrogallic. If a wet collodion plate be washed, flooded with a solution of ammonia and hydrokinone, and exposed in the camera, the picture will make its appearance on the plate during the exposure, a result which is not to be obtained either with ferrous-oxalate or alkaline pyrogallic.[2] The results of experiments that I have made with this substance are quite in accordance with Capt. Abney's statement. A 4 per cent. solution to which from 2 to 4 drops of ammonia have been added, brings out more detail, and gives a more brilliant negative, than a powerful pyrogallic developer, made up according to the formula in the foot-note,[3] and

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[1] *Photo. News*, 1880, xxiv., 345.

[2] Capt. Toth and myself found that a plate treated with either potassic ferrous, or ferric oxalate was exceeding insensitive when dry, probably owing to the orange and green solutions absorbing too much actinic light.

[3]

Pyrogallic acid (1·10)	1 c.c.
Potassium bromide (1·10)	1 c.c.
Ammonia..	2 drops
Water	50 c.c.

only requires about nine-tenths the exposure. More ammonia may be used than is given above, but there is a danger of fog if too much be employed. Potassium bromide deprives the developer of its energy to a great extent. In the commercial samples of hydrokinone that I have tried, I have found variable quantities of free acids, such as sulphuric and sulphurous acids. It is worth noticing that ferrous-oxalate requires less restraining than alkaline pyrogallic, and hydrokinone hardly any at all.

The colour produced by this developer is somewhat similar to ferrous oxalate, and contains none of the brown given by alkaline pyrogallic. The superiority of hydrokinone as a developer is not sufficiently marked to militate against its present high price, but in case the latter is reduced, it may be borne in mind as an excellent developer.

Resorcin and pyrocatchin are analogous to hydrokinone. Their composition is generally $C_6H_4(OH)_2$. A developer made up with 2 or 3 drops of ammonia to every 20 c.c. of a 5 per cent. aqueous solution of pyrocatchin gives a good negative, but requires a longer exposure than either ferrous oxalate or pyrogallic acid. An increase of ammonia gives a tendency to fog.

Resorcin is inferior in energy to the other two substances mentioned above. A developer consisting of 20 c.c. of a 5 per cent. solution of this body requires as much as 20 drops o ammonia to develop a negative, and requires two or three times the exposure of alkaline pyrogallic. Resorcin has an antiseptic action, and may be found useful for preventing decomposition. It is more soluble in water than phenol, thymol, or salicylic acid.

Phloroglucin, which is analogous in composition to pyrogallic acid, possesses very little reducing power, and is not of much use for development of gelatine plates.

Hydrosulphite.

The developing power of hydrosulphite has been familiar for some time, the best salt for the purpose being sodic hydrosulphite. To test the capacity of this developer I digested a strong solution of sodic sulphate with powdered zinc over-night, so that the precipitate which was formed might stand in cold water, and any tendency to heating be avoided.

In a concentrated form, this developer is quite as energetic as either pyrogallic acid or ferrous oxalate, and when used fresh requires about the same exposure. It gives delicate and harmonious negatives of a clear gray colour, and does not need any restrainer. There is, however, a great inconvenience attaching to the use, owing to the intolerable smell of sulphurous acid given off during development. Diluted solutions have little developing power, and give no density.

IV.—ADDITIONS OF SOLUBLE BROMIDE, CHLORIDES, AND IODIDES TO DEVELOPERS.

In the development of gelatine plates, potassium bromide is invariably added in order to keep the development under control, and check a tendency to fog. The use of a soluble iodide or chloride has been suggested for the same purpose, but neither of these bodies possesses the same restraining power as the bromide. With the former there is a great tendency to flatness and want of contrast. Carey Lea finds that an addition of potassium iodide to ferrous oxalate gives a reddish tone to the finished negative, while chloride gives much the same colour as the bromide.

CHAPTER VII.

INTENSIFICATION OF GELATINE NEGATIVES.

GELATINE plates often require intensification. This operation has to be performed after fixing, as it is impossible to judge of the density of the picture, owing to the want of transparency of the negative. Opinions as to the best means of intensification are very much divided. This operation is much more difficult than in the case of collodion plates, where we have to deal with a vehicle unacted on by the various intensifying agents. Gelatine, on the other hand, combines with many of the substances used to form fresh bodies liable to alteration in presence of light, and resulting in a bleaching or change of colour in the negative. In reviewing the various methods of intensification, I shall refer to the older methods as well as to the more recent, and at the same time offer such remarks on the various formulæ as my experience has suggested.

1.—*Mercuric Chloride and Ammonia.*

The negative, after fixing and washing, is flooded with a 4 or 5 per cent. solution of mercuric chloride, or a saturated aqueous solution which represents about 7 per cent. When the colour of the negative has changed to a clear grey, it is washed, and flooded with a weak solution of ammonia, which gives a black colour to the negative.

This is a very old method, and is to be recommended. An alcoholic solution of mercuric chloride is not advisable, as it eats out the half-tones, and makes the negative hard.

England's intensifier is similar to this. Instead of the formula given above he employs—

Mercuric chloride	1 part
Ammonic ,,	1 ,,
Water	20 to 24 parts

This form of intensification is valuable in portraiture, as it does not affect the half-tones. The colour is black by reflected light, and dark brown by transmitted light; but, unfortunately, the colour is apt to bleach, if but slightly, after exposure to light.

2.—*Mercuric Chloride and Sodic Hyposulphite, Ammonium Sulphide, or Potassium Cyanide.*

This method differs from those above in the employment of sodic hyposulphite or potassium cyanide, instead of ammonia. Wilde recommends that after treating a negative with England's mercuric chloride formula, it should be flooded, after washing, with the following:

Ammonia	1 part
Sodic hyposulphite	1 ,,
Water	12 to 20 parts

Ammonium sulphide gives a denser negative, but is not so satisfactory generally as the methods already given.

3.—*Mercuric Bromide and Sodic Hyposulphite* (*Wilde*).

The negative is well rinsed after fixing, and flowed over several times with a 25 per cent. solution of mercuric bromide, and afterwards with a concentrated solution prepared as follows:—

Mercuric chloride	12 grammes
Water	600 c.c.
Potassium bromide	18 grammes
Water	66 c.c.

In a few minutes the negative assumes an uniform opal colour, somewhat like a weak silver print. It is then rinsed, and laid in a very weak solution of hypo, and in a few seconds a brilliant negative is obtained. Wilde, however, generally employs the method given in section 1.

This intensifier is less vigorous than mercuric chloride and ammonia.

4.—*Mercuric Chloride and Cyanide of Silver* (*Monckhoven*).

A similar method to this was suggested by Burton in the *Year-Book of Photography* for 1873, ammonic chloride being employed instead of potassium bromide. The negative is washed and laid in the No. 1 solution, until the proper density is obtained, the limit being reached when the whole of the negative is white. It is then laid in the No. 2 solution, which gives a dark colour to the plate.

No. 1—	Mercuric chloride	20 grammes
	Potassium bromide	20 ,,
	Water	1 litre
No. 2.—	Silver nitrate	20 grammes
	Water	½ litre
	Pure crystallized potass. cyanide	20 grammes
	Water	½ litre

The cyanide solution should contain an undissolved precipitate of flakey silver cyanide. If the negative remain too long in the No. 2 solution the deposit is attacked, and the density reduced. Probably, owing to this, Monckhoven recommends in his recent work on gelatino-bromide of silver the employment of the mercury and ammonia intensifier.

5.—*Mercuric Iodide.*

The negative is fixed, washed, and treated with the following solution :—

Mercuric chloride	1 gramme
Potassium iodide	3 grammes
Water	200 c.c.

The plate intensifies to a brownish tone, without the shadows being in any way effective. This is a good intensifier, but, unless the mercuric chloride has been well washed off, the negatives are apt to turn yellow by exposure to light. On the whole, the best plan with mercury is to follow up with ammonia, and wash well. The resulting colour is all that can be desired, and the negative is not liable to any subsequent change.

EDWARDS' MERCURY AND HYPOSULPHITE OF SODA INTENSIFIER.

This intensifier consists of a mixture of mercuric chloride, potassium iodide, and hyposulphite of soda, and its merits are highly spoken of.

No. 1.—Mercuric chloride...	4 grammes
Potassium iodide	6 „
(dissolved in 65 c.c. water)	
Water	200 cub. cents.

The red precipitate formed by No. 1 solution is dissolved away by an addition of 8 grammes of hyposulphite of soda in 65 c.c. of water. It is better, as Edwards has since advised, to increase the proportion of iodide from 8 to 12 grammes, so that the red precipitate of mercuric iodide is again redissolved before the addition of the hyposulphite. This gives a clear solution, while the former turns thick after a short time. In either case, however, the intensifying action is equally energetic. This method is very convenient, owing to the fact that the hyposulphite left in the film, after fixing, need not be entirely eliminated; but it is better to remove that which remains on the surface as much as possible. This solution is equally available for collodion plates, works rapidly, and gives a brown tone to the resulting negative. The addition of more hyposulphite imparts a better colour, but renders the action of the intensifier slower. The solution gets thick by keeping, and deposits a black precipitate; but it retains its energy for a long time. The black precipitate consists of iodide of mercury, metallic mercury, and mercuric sulphide. If kept in the dark, it separates into solution of mercuric iodide in hyposulphite of soda and pure yellow mercurous iodide. Exposed to light the precipitate is reduced, and gets darker in colour. Negatives intensified by this formula are not permanent, but, after exposure to light, get yellow, and eventually fade, a change which destroys the printing power of the negative. It is always better, however, that the negative should get lighter rather than darker.

7.—*Intensification with Uranium.*

This method was published in 1865, for use with collodion plates; but it is equally valuable in the case of gelatine work. The negative, after fixing, is well washed, and flooded with a solution containing 1 gramme of uranium nitrate and 1 gramme of potassium ferricyanide in 100 c.c. of water. Barlow recommends that the plate should be flooded with a 1 per cent. solution of uranium nitrate, which should be allowed to remain on the plate for about half a minute or so, and then poured back into the measure, into which a few drops of a 2 per cent. solution of potassium ferricyanide has previously been added.

The mixed solutions are then poured over the plate, and if sufficient intensity is no obtained, more potassium ferricyanide may be added. The intensity is easily controlled, the colour of the resulting negative being brownish red. The mixed solutions should show no signs of cloudiness, otherwise the sample of potassium ferricyandide is not pure, or has become converted into the ferro-cyanide by long exposure to light. A plate intensified in the manner described, and well washed until the wash-water gives no trace of blue colour with ferrous-chloride or ferrous sulphate, is very permanent, much more so than when mercury has been employed. If any trace of potassium ferricyanide remains in the film, the negative will turn brownish yellow after it has been much printed from.

8.—*Intensification with Silver Nitrate.*

Owing to the liability of gelatine plates to develop red stains during intensification with silver, the practice has been attended with some difficulty. Consequently, photographers employ principally mercurial intensification, which is not subject to this defect, although not free from a tendency to bleach in some cases, and gets darker in others when the plates are exposed to light. The latter defects have been patent for some time, and there is a general desire to adapt the old method of silver intensification to gelatine plates. It is imperative, in the first place, to remove all traces of the fixing solution from the film. This is not easy to do by washing when hyposulphite of soda has been employed, and it is preferable to decompose it by soaking the plate for five or ten minutes in a weak sherry-coloured solution of iodine in iodide of potassium; or in a (1-1000) solution of potassium permanganate. A concentrated solution of alum removes hypo best of all.

Abney recommends a (1·30 up to 1·80) solution of hydrogen peroxide as a means of destroying the last trace of hyposulphite of soda. A mixture of ferrous sulphate and silver nitrate is rather better than pyrogallic acid and silver nitrate, as the latter is apt to discolour the negative. As a restrainer, either citric, tartaric, or acetic acid may be employed with the addition of gelatine or sugar. The silver nitrate solution can be rendered acid with nitric acid.

The formula given for silver intensification by Wratten and Wainwright is a very good one:—

A.—*Gelatine Solution.*

Gelatine	1 gramme
Acetic acid	12 c.c.
Water	20 c.c.

B.—*Iron Solution.*

Ferrous sulphate	3 grammes
Water	100 c.c.

C.—*Silver Solution.*

Silver nitrate	1 gramme
Acetic acid	60 drops
Water	50 c.c.

Pour on the plate 30 cubic centimetres of the (B) solution, to which 40 drops of A have been added. Allow this to remain on the plate for a short time, and then pour back into the cup; add a few drops of C, and then pour on to the plate again. The negative will gain intensity slowly and steadily.

Abney recommends, in the PHOTOGRAPHIC NEWS,[1] a solution containing ferrous sulphate 1 gramme, citric acid 2 grammes, in water 100 cubic centimetres, to which a few drops of a 20-per-cent solution of silver nitrate is added. The first solution is improved, I think, by the addition of 1 or

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[1] 1880, xxiv., 814; and Abney's "Practical Working of the Gelatine Emulsion Process," 1880, 61.

2 grammes of sugar, and the silver nitrate by 4 to 5 per cent. of glacial acetic acid. Ratcliffe suggests[1] the addition of albumen to the iron solution; but I find it gives a precipitate when mixed with the silver nitrate.

Intensification with pyrogallic acid and silver is performed in the same manner as above. Abney recommends a solution of 0·4 grammes pyrogallic acid, and 0·4 grammes citric acid to 100 cubic centimetres of water. Silver nitrate solution should be 4 per cent.

Jarman employs a concentrated solution of pyrogallic acid—pyrogallic acid one gramme, citric acid 1·3 gramme, in water 100 cubic centimetres; but he destroys its excessive energy by adding 2 drops of strong nitric acid to every 8 cubic centimetres of solution, and then adds 6 drops of a 5 per cent. solution silver nitrate. In order to make sure that no free silver is left in the film,[2] the plate is laid, after intensification, in a solution of common salt, or in a very dilute solution of hydrochloric acid, which has also the effect of removing any stain caused by the pyrogallic acid. The last trace of silver can now be entirely removed by the use of a weak fixing solution. In intensifying by any of the methods given above for silver intensification, a good deal of the solution should be used, and kept constantly in motion, otherwise red fog is liable to make its appearance.

9.—*Concluding Remarks.*

A gelatine plate may be flooded with a solution of iodine in iodide of potassium, then washed, and flooded with a weak solution of ammonium sulphide. The negative assumes a permanent dark colour. Platinum, palladium, and gold are not

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[1] Abney's "Practical Working of the Gelatine Emulsion Process," 1880, 62.

[2] The fact that gelatine combines with silver, and forms a compound insoluble in water, was stated in 1859, *Journ. Photo. Soc. of Gt. Brit.*, vi., 308

much used in connection with intensification of gelatine plates. A negative treated with chloride of gold must be well washed otherwise the plate will turn red on exposure to light.

Intensification with lead is useful in gelatine work; but it is impossible to obtain absolutely clear plates, unless the lead is thoroughly removed by washing, before the plate is treated with potassium bichromate or ammonium sulphide.

The question naturally suggests itself at the conclusion of this subject as to which is the best intensifier to make use of with gelatino-bromide plates? And it is one which it is impossible to answer absolutely. It is necessary, to begin with, to take into consideration the quality of the plates employed, as all kinds of gelatine plates do not behave alike under the action of an intensifier. As the manufacturer should know best the quality of his own production, it is as well to adhere to the special instructions, if any, sent out with the plates.

For portraiture, where a good deal of intensity may be necessary, England's method with mercuric chloride and ammonia may be recommended, as the negatives so treated will admit of several dozen prints being taken off without showing signs of bleaching. This method is very favourable for thin weak negatives, as it tends to give an increase of contrast.

Edwards' intensifier, and the method requiring the use of mercuric iodide and ammonia, are more permanent, but as they both tend to reduce contrast, they should not be used for very flat negatives. The former, consisting, as it does, of a single solution, is easily used, and the growth of intensity can be carefully watched. The latter appears to be the more permanent.

Selle's uranium intensifier, already described, is highly to be recommended, and is very permanent. A negative which will not acquire sufficient intensity with this method may be laid aside as useless. Intensification in the shadows may be successfully obtained by treating a plate for a short time with a weak solution of uranium; if the solution be too strong, or the application be prolonged, the negatives may probably become too hard.

With regard to silver intensification, I must say that, in spite of all precautions, it is not to be depended upon. With gelatine plates there is no certainty in the method. I should never attempt to employ it in the case of a valuable negative, nor recommend anyone else to do so. It requires no special experience to attain some measure of success with other methods, especially Nos. 1, 5, 6, 7; at all events, there is little chance of ruining the negative.

CHAPTER VIII.

THE VALUE OF GELATINE PLATES FOR WORKS OF PRECISION.

WITH the view of determining to what extent gelatine plates could be depended upon for work requiring extreme precision, I made a set of experiments which were so satisfactory as to leave no doubt of the suitability for this purpose of good gelatine plates.

I.—ERRORS CAUSED BY EXPANSION OF THE FILM.

I have already alluded to the expansion and distortion to which inferior gelatine emulsions are liable during development, and, as a means of proving whether a film which apparently adheres to the plate suffers any expansion which could be detected by microscopical measurement, I made the following experiment.

A fine net-work was scratched with a diamond on a sheet of glass, and a number of gelatine plates prepared in various ways were exposed under it and developed, half with alkaline pyrogallic acid, and half with ferrous oxalate. Some of the plates had been coated without cleaning, others had received in different cases substrata of water-glass, or gelatine and chrome alum. In all cases the films adhered well, and showed no signs of frilling. When the plates were examined against the original, there was no expansion or contraction visible, although the means of detection that I employed were delicate enough to detect a variation of $\frac{1}{6000}$ in the dimensions of the line. We may, consequently, conclude that, as regards expansion of the film itself, good gelatine plates are thoroughly reliable for this class of work.

II.—CHANGE IN DIMENSIONS OF LINES OWING TO ELECTROLYTIC ACTION.

It still remained to decide whether any change occurred in the dimensions of lines owing to electrolytic action during development.

The continuous reduction of bromide of silver under the action of a developer takes place, laterally as well as downwards, and the former is under certain circumstances quite capable of being recognised. A series of black lines were drawn as sharply as possible, and copied on a gelatine plate. The dimensions of the lines, when compared microscopically with the original, showed no change of any note when moderately enlarged, and after a development lasting over about three minutes.

Much the same result obtained when the development was protracted to thirty minutes, so long as no trace of fog made its appearance during the progress of the operation. For instance, a line measuring in the original 0·28 m.m. showed no perceptible change after a development of three minutes, but, on the other hand, when the development lasted for thirty minutes with ferrous oxalate, the edges of the line, which in the negative were transparent, had slightly increased, and the line now measured from ·198 to ·2 m.m. This contraction, however, is of so little consequence as to be immaterial.

The experience was much more unfavourable when, owing to long development, fog spread over the whole plate, a circumstance to which one is extremely liable with alkaline pyrogallic. Examined under a microscope, the edges of the line were not sharp, and the silver film forming the boundary of the line increased towards the centre of it. We may conclude from these results that in making an exact reproduction on gelatine plates of sharply-defined lines, the development should be got over as quickly as possible, and should under no circumstance be continued after fog has set in.

CHAPTER IX.

PREPARATION OF HIGHLY SENSITIVE GELATINO-BROMIDE EMULSIONS.

THREE methods will be found described below of preparing extremely sensitive emulsions, as the result of the numerous experiments that I have made on this subject. The first method consists in the addition of ammonia to the bromide of silver in its original state, with the view of producing the sensitive modification more rapidly than in Monckhoven's process.[1]

The second consists in treating the emulsion after boiling with ammonia for half-an-hour at a temperature of 35° C., and gives the most sensitive results of any method that I have tried.

The third method is the original and safer one of long digestion at low temperature.

1.—PREPARATION OF AN EMULSION WITH AMMONIACAL SILVER NITRATE.

This process gives extremely sensitive plates, at least six or seven times as rapid as wet collodion. The operations

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[1] Monckhoven's earlier method consists in addition of 5 c.c. ammonia (sp. gr. 910) to every 300 c.c. of emulsion before digestion. In his more recent pamphlet he recommends, however, that the emulsion should be simply boiled; but he also gives a method of treating the emulsion with ammonia for getting rid of grease spots. A summary of other methods of compounding emulsions will be found in Abney's "Practical Working of the Gelatino-Bromide Process" (Piper and Carter, London).

are exceedingly simple, and require only a reliable dark room, a saucepan, spirit lamp, and thermometer. The plates are very clear and brilliant, suitable alike for landscapes or portraiture, and give sufficient density for reproduction from linear drawing at one operation. The following directions will be found the best.

24 grammes of pure air-dried potassium bromide are dissolved in 300 c.c. of distilled water, 30 to 45 grammes of gelatine introduced, and the whole, after soaking for about a quarter of an hour, is placed in a water bath at a temperature of 35° to 45° C., till the gelatine has dissolved, and the solution is clear. 30 grammes of silver nitrate are then dissolved in 300 c.c. of water, and ammonia is added drop by drop, until the precipitate first formed is redissolved and the solution clear.[1] These operations can be carried on in daylight. Now, by as weak a ruby light as possible, add the silver solution to the gelatine gradually, and allow it to cool down to 35° C., shaking well after the addition has been made, and at intervals, and rinse out the remains of silver in 50 c.c. of water. Then replace the bottle in the water bath, which should be at a temperature not exceeding 35° C.; let it remain for from half to one hour, allowing the water in the bath at the same time to cool down gradually. The temperature may be allowed to sink as low as 25° C. without any fear of the gelatine setting; but the quantity of water should be sufficient to prevent the temperature falling lower. In this method the purity of the chemicals used is not of so much consequence as in the second method. The potassium bromide or the gelatine may be alkaline, and there is no absolute necessity for the silver nitrate to be neutral. The specific gravity of the ammonia is immaterial; but it should be fairly strong, and sufficient added to redissolve the precipitate. In adding ammonia to

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[1] According to Prescott, the following reaction takes place; –

$$2AgNO_3 + 4NO_4OH = (NH_3Ag_2)O + 2NH_4NO_3 + 3H_2O.$$

the potassium bromide instead of to the silver nitrate,[1] we have no such test to guide the required amount, and as the same sensitiveness can be obtained by either method, the latter is preferable. Great care should be taken in adding the ammonia that the temperature does not rise too high, and that the water bath, during digestion, does not become too hot, otherwise fog is certain to ensue. The temperature should never exceed 40° C.

When the digestion is completed, the emulsion may be poured into a porcelain dish, and the latter placed in cold water to hasten the setting. When completely set, it is pressed through coarse canvas, the meshes of which should be about 2 to 3 m.m. apart, and then suspended in a bag and washed either in frequent changes of water, or, better still, in running water for two, four, or five hours. As the emulsion takes up a good deal of water during the washing, the latter must be removed either by allowing it to drain for some time, or the excess may be got rid of either by gentle pressure or by pouring alcohol over the emulsion. In the latter case only half the ordinary amount of alcohol should be added to the emulsion after filtering. The emulsion may now be melted and filtered, or any sediment may be allowed to subside to the bottom. If the emulsion is to be preserved, an antiseptic should be added, consisting of ·2 grammes of salicylic acid, dissolved in 5 to 6 c.c. of alcohol to every 100 c.c. of emulsion. The same weight of oil of thyme—or, best of all, carbolic acid—may be substituted. The alcohol has a favourable action in assisting the setting of the emulsion.

The proportions of potassium bromide to silver nitrate employed should not be less than 4 or 5, otherwise there is a danger

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[1] If the gelatine and potassium bromide be dissolved in the presence of ammonia, and then the silver nitrate added, the action of the ammonia on the gelatine should not be prolonged to the same extent. The best way is to add the ammonia immediately before the addition of the silver nitrate to the gelatine.

of fog. The difficulty of determining the proper proportions depend on the fact that if too much bromide be employed, the sensitiveness is reduced; if too little, there is a danger of fog. If an emulsion containing a very small excess of soluble bromide be prepared without ammonia, and digested for several days at a temperature of 35° or 40° C., the process of modification proceeds rapidly, and, owing to the low temperature employed, there is very little danger of decomposition. If, however, the operation is shortened by boiling or addition of ammonia, an excess of soluble bromide is very useful to counteract the natural tendency to fog. In the case of long digestion, an excess of soluble bromide retards, but does not prevent the attainment of great sensitiveness.

The conversion of the insensitive into the sensitive modification takes place very rapidly if the directions given above be followed out. Even at a temperature of 25° C. the operation is generally complete in fifteen or twenty minutes. If a drop of the emulsion, examined on a strip of glass, transmits blue light, the digestion may be stopped, and it will generally be found that prolonging the digestion over thirty minutes does not give material increase of sensitiveness, although, if the temperature be properly controlled, it may be continued for three hours without any decomposition.

If the solutions are too hot when the emulsion is prepared, or the proportion of gelatine be too small, or the silver solution not sufficiently dilute, a coarse-grained emulsion, without any corresponding increase of sensitiveness, will be the result. This kind of emulsion would be useful in several of the heliographic processes, and can be obtained by dissolving the quantity of silver nitrate given above in 100 c.c. of water instead of 300 c.c.

As there is no danger of the emulsion losing its setting powers under the low temperature employed, it is best to add all the gelatine at once. In emulsifying with ammonia, it is never advisable to add a second quantity of gelatine to the emulsion after digestion, owing to the renewed heating which it entails. When the action of the ammonia is too prolonged, especially in summer time, frilling is very apt to ensue. Methods have already been given for curing this defect.

The washing of the emulsion should be conducted with the greatest care, as it is absolutely impossible to attain full sensitiveness in the presence of a considerable excess of soluble bromide; and if any trace of ammonia be left behind, it exercises a caustic action, and combines with any salicylic acid which may afterwards be added, so as to reduce its antiseptic properties. It is worth noticing that an unwashed emulsion prepared without ammonia will keep sound for a long time without requiring the addition of an antiseptic.

In proportioning the amount of gelatine to the sensitive salts, it was laid down in a leading article of the PHOTOGRAPHIC NEWS that if a hard gelatine, possessed of great powers of resistance, be employed, less is required than when a softer sample is made use of. A small proportion of gelatine is to be recommended, for the following reasons:—The emulsion when broken up into small pieces does not absorb so much water during washing. When the emulsion is rich in bromide of silver, there is no necessity for using thick films, which, besides being liable to frill, take much longer to dry than thin ones. If, on the other hand, the proportion of gelatine be too small, the bromide of silver is coarse in the grain, and sinks to the bottom of the emulsion. In preparing a hard, quick-acting emulsion, we generally employ a large proportion of potassium bromide, a given quantity of gelatine, and one-and-a-half times its weight of silver nitrate. Dr. Van Monckhoven rightly remarks that a large proportion of gelatine gives a soft image; a small proportion a denser but harder picture.

Commercial samples of gelatine emulsion often contain a very small amount of silver in proportion to the gelatine. This, of course, places the purchaser of such an emulsion to the disadvantage of using thick films, with their attendant disadvantages, and of requiring, in consequence, more emulsion for any given number of plates to be coated. If manufacturers would state what percentage of silver their emulsions contained, the high price of one rich in silver would easily be understood, and photographers who purchase emulsion would not, as they naturally do, buy the cheapest sample, which usually contains the least amount of silver.

II.—PREPARATION OF AN EMULSION BY BOILING, AND SUBSEQUENT DIGESTION WITH AMMONIA.

This method gives more sensitive plates, but requires greater care, than the preceding. It depends on the fact that the sensitive modification of bromide of silver forms very rapidly at temperatures between 60° C. and 100° C., and that the sensitiveness of such an emulsion, in itself very great, can be still further increased by subsequent treatment with ammonia at a low temperature.

The proportions of silver, &c., are the same as those previously given:—24 grammes of potassium bromide, which should not be alkaline, are dissolved in 300 c.c. of water, in a strong glass bottle,[1] and 30 to 45 grammes of gelatine introduced, and the whole, after soaking for some time, is dissolved in hot water, at a temperature of 60° C. or 70° C.; the remaining operations must be conducted in the dark room. To the warm solution of bromized gelatine add 30 grammes of silver nitrate, previously dissolved in 300 c.c. of water. The latter may also be warmed

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[1] In preparing emulsion on a large scale, a hock bottle or an earthenware jar is very convenient, as they can be sealed up so as to be quite light-tight without any danger of bursting during the cooking of the emulsion. When there is no necessity for using a light-tight bottle, any ordinary bottle may be employed, with a groove cut in the cork to allow of the escape of the steam.

over the water bath; but there is no absolute necessity for this proceeding. Now wrap the bottle in a thick cloth, and shake well, taking care that the cork is not blown out by the steam. The remainder of the silver may be rinsed out in 50 c.c. of water.[1] During the boiling which follows, the cork must not be pushed in too tightly, otherwise the pressure of steam might break the bottle.[2] The best way is to replace the cork during boiling by another in which a small groove has been cut for the escape of the steam. The bottle containing the emulsion is put into a saucepan, covered by a tightly-fitting lid, and the spirit lamp or gas jet light below, care being taken that not even the reflected light from the flame falls on to the emulsion. The water bath, which should contain hot water, can soon be brought to boiling point, at which temperature the emulsion should remain for twenty or thirty minutes, after which it may be allowed to cool down.[3]

The emulsion at this stage will be found extremely sensitive, and *can be used as it is;* but by further treatment with ammonia, it is possible to increase the sensitiveness considerably.

When the temperature has fallen to about 20° C., 8 c.c. of strong ammonia (sp. gr. ·910) are added, and the emulsion is digested for half-an-hour or an hour at a temperature of 35° C.

Finally, 1 to 2 grammes of potassium iodide, dissolved in a little water, is added to produce a clearer film.

[2] A roll of linen will prevent the bottle coming in contact with the heated surface of the bottom of the saucepan.

[3] When large quantities of emulsion are being prepared, the boiling should be continued longer. The necessary time of boiling must be reckoned from the moment that the emulsion reaches a temperature of 90° C. If the emulsion is very acid, such as occurs when ammonium bromide is employed, the boiling may be continued for an hour without damage, and with a resulting increase of sensitiveness. But as gelatine boiled in the presence of an acid is apt to decompose, only a small portion of the gelatine should be used, and the bulk added afterwards.

to 37° C. After this the emulsion is ready for washing, which may be carried out in the same manner as already described.

An emulsion prepared in this way is, perhaps, one-fifth more sensitive than one prepared according to Method I. It gives well-balanced, harmonious pictures, free from any tendency to hardness. The picture comes up readily under the developer, and the details in the shadows should be fully developed before the high-lights are too dense. I consider emulsions produced by this method specially suitable for portraiture, although they do not give such absolutely clear glass in the shadows as can be obtained by the first method. In preparing an emulsion by Method II., extreme care should be exercised in the choice of materials.

The gelatine and bromide should not be alkaline, otherwise there is danger of fog during the boiling. Warming the bromized gelatine to 60° C. or 70° C. as recommended, before the introduction of the silver nitrate, hastens the operations considerably. Half-an-hour was fixed on as being the most suitable period for the boiling, a quarter of an hour being hardly sufficient; while if the operation was prolonged to three-quarters of an-hour, fog sometimes ensued. Some samples of gelatine will admit of longer boiling than others. Generally speaking, the emulsion may be boiled so long as it remains clear, and the longer it is boiled the more sensitive will it be.

In digesting an emulsion with ammonia, special care must be taken that the temperature does not exceed 40° C. Generally speaking, half-an-hour's digestion will be sufficient, but the operation can be continued for an hour, and even two hours, without

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[1] If a difficulty is experienced in procuring neutral, or slightly acid, materials, the warm solution of potassium bromide and gelatine may be cautiously acidified with dilute acetic acid. The condition of the mixture must be only very slightly acid, otherwise the setting power of the gelatine will be impaired.

danger, and there is more certainty that the desired sensitiveness will be attained. Besides this, the subsequent treatment with ammonia compensates for any defect in the boiling during the first part of the process. The same precautions which I recommended under Method I., in regard to the addition of ammonia, are applicable in this case. In both methods it is directed that all the gelatine should be added at the outset. With some samples of gelatine easily acted upon, it may be found necessary only to add part of the gelatine at first, and the remainder after the digestion is completed. In developing these highly sensitive emulsions, alkaline pyrogallic may be employed; but I can recommend ferrous oxalate as giving clear brilliant pictures.

METHOD III.—PREPARATION OF AN EMULSION BY DIGESTION AT LOW TEMPERATURES.

Although the methods given above have never failed, either in my hands or in those of careful experimenters, yet, owing to the extreme care required in the manipulations, and the danger of fog from the use of unsuitable materials, I have thought it best to give another formula which may be absolutely relied on even in unskilled hands.

After what has already been said on the subject, I may give the formula in a few words:—24 grammes of potassium bromide and 40 grammes of gelatine[1] are dissolved by heat in 300 c.c. of water, and, as soon as solution in complete, the temperature of the mixture is raised to 40° C. or 45° C., and a solution of 30 grammes silver nitrate in 300 c.c. water introduced. The emulsion is placed in a water bath at a low temperature, viz., 32° C. to 35° C., and digested at this temperature.

If an emulsion is required about as sensitive, or twice as sensitive, as wet collodion, it may be used after six to twelve

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[1] It is well to keep back half the gelatine till after digestion.

hours' digestion. Such an emulsion is very well adapted for landscapes or interiors, and should find a place in every studio.

If a more sensitive preparation is required, the digestion may be continued for three days at a temperature of 35° C. The resulting emulsion is very sensitive, and well adapted for portraiture, as it gives soft, harmonious negatives. Either ferrous oxalate, or Edwards' glycerine developer, is suitable as developer; the former giving rather more contrast than the latter. This emulsion may be looked on as one of normal sensitiveness. For exceptional cases, where still greater delicacy and sensitiveness are required, the emulsion is digested for four or five days at a temperature of 35° C.; or, still better, to the quantity of emulsion (about 600 c.c.) given by the formula, 8 c.c. of ammonia (sp. gr. ·910) are added. The emulsion should be at a temperature of 35° C. when the addition is made, and then be digested for half-an-hour to one hour at the same temperature.

No doubt the best method of washing the emulsion is to break it up into small pieces; but as, in this state, it absorbs a large quantity of water, I give a method recommended by Dr. Heid. The emulsion is poured out, after digestion, into a tall square glass bottle, which should not be more than a quarter full at the most. The bottle is then laid on its side, and the emulsion allowed to set. When it has set, the bottle is filled completely with water, tightly corked, and laid on its side so that the part covered with emulsion is uppermost. The water should be changed repeatedly during twenty-four hours, after which the emulsion is ready for coating; 30 to 50 c.c. of alcohol should be added previously, and, if the emulsion is to be kept, an antiseptic may be added.

CHAPTER X.

FAILURES IN THE GELATINO-BROMIDE PROCESS.

In working with gelatine emulsion, there is always a danger of chemical or light fog, due in the first case to faults in the preparation or development of the emulsion, and in the second to admission of light during some portions of the process.

In the following chapter I have enumerated most of the possible causes of failure under the several processes, commencing from the coating of the plates down to the varnishing of the finished negative.

1. *The Emulsion becomes Fluid in the Bottle.*—This defect is often due to the want of an antiseptic, such as salicylic acid, carbolic acid, thymol, &c., in the emulsion. The emulsion under the circumstances refuses to set. The setting powers can be restored by the addition of fresh gelatine; but the presence of any decomposed matter is apt to give very foggy plates.

2. *The Emulsion is Thin, and Permits some of the Bromide of Silver to Separate to the Bottom of the Flask.*—This may arise from too small a proportion of gelatine having been employed, the consistency of the solution being insufficient to retain the bromide of silver in suspension; or it may be due to a tendency to decomposition. The remedy in either case will be to stir in thoroughly fresh gelatine in the proportion of 2 grammes to every 100 c.c. of emulsion.

3. *The Emulsion Turns Brown and Grey.*—This often occurs when the emulsion has been exposed for some time to white light, but the change will probably only affect the surface of the emulsion, and the interior will still be sensitive and fit for use.

4. *The Emulsion Flows Irregularly* over the plates.—This will probably be due to the want of a substratum. A weak solution of water glass (1-200) may be used, or a syrup of sugar and water, or albumen. Gelatine emulsion will not flow well over a collodion substratum unless a small quantity of glycerine, about 2 per cent., is previously added.

5. *Waves and Irregular Marks* occur during coating, principally in winter time, when the plates are too cold, or the emulsion not sufficiently fluid. The marks do not show after fixing. If the plates, on the other hand, are too hot, streaks are formed, which show in the finished negative. The plates should be slightly warmed, and the emulsion kept in water at a temperature of about 50° C. or 60° C.

6. *Air-Bubbles* which form on the surface of the film during coating can easily be avoided by pouring back the excess of emulsion into a separate vessel. The best form of vessel to employ is an earthenware tea-pot wrapped up in a thick cloth.

7. *The Emulsion Refuses to Set* when poured on to the plate.

(*a*).—The temperature of the coating room may be too high; if so, the plates should be laid after coating on a metal plate or a stone slab, when they will set in a few minutes, and the film will not melt again so readily as it otherwise would.

(*b*). The proportion of gelatine in the emulsion may be deficient. This may be remedied by the addition of 2 or 3 grammes of fresh gelatine to every 10 c.c. of emulsion, and, after standing for a few hours, the latter should be heated to ensure complete solution.

(*c*). The want of setting power is more often caused by a decomposition of the emulsion, consequent on too long a boiling, too high a temperature, injudicious use of ammonia, or frequent melting and setting of the emulsion, which is especially injurious to a gelatine of inferior quality. This want of setting power often gives rise to frilling and blisters, which may be avoided by the addition of a small quantity of the alum and glycerine solution described in Chapter III.

8. *Spots and Small Rings*, which are very apparent in the finished negative, are due principally to irregular drying of the plates. The drying may have been prolonged too long owing to variations in the state of the atmosphere or temperature, or the same defect may arise from having the drying cupboard too hot, and opening the door frequently while the plates are drying.

9. Gelatine films which have been dried by soaking in alcohol frequently crack owing to the contraction of the gelatine being too rapid. At other times faint marks make their appearance, which are visible in the finished negative.

10. *Mildew* occurs when the plates have been kept in a damp place. An emulsion to which an antiseptic has been added is not liable to this defect.

11. *The Plates are very Slow in Developing*, or develop irregularly, when they have been kept for a long time in a very dry place. In developing such plates, they should be previously soaked for some time in water. The emulsion may contain too much alum or chrome alum, in which case the addition of a few drops of glycerine will improve its absorptive power. Such an emulsion is best treated with the pyrogallic developer, and before the addition of the pyrogallic acid a dilute solution of ammonia may be allowed to act on the plate for a few minutes. If the films are very hard, they may be soaked for a few minutes in water at a temperature of 30° C.

12. *If the Plate, on Fixing, appears Fogged*, the mistake may have been caused by over-exposure, careless development, employment of a faulty emulsion, or admission of white light at some stage of the operations.

(*a*). The part of the plate protected by the rebate of the frame should be examined; and if this be free from fog, the fault has been due to over-exposure.

(b). If, however, the whole plate fogs over during development, we may suspect that light has been admitted. The camera and dark slides should be carefully examined, as well as the connection of the flange of the objective with the front of the camera. To test the quality of the ruby glass employed in the window or lantern, half a gelatine plate should be carefully covered over, and the remaining half exposed for three to five minutes to the light passing through the ruby glass. When treated with a fresh developer, both portions should fix out quite clear. If the exposed half fogs over, while the unexposed portion remains clear, the glass may be considered unsafe.

(c). Fog may be due to decomposition of the gelatine, caused either by cooking the emulsion too long, use of too high a temperature, addition of too much ammonia, or the employment, under certain circumstances, of materials having an alkaline reaction. The remedy for this so-called chemical fog consists in the addition of a few drops of tincture of iodine, or treatment of the emulsion, after it has been pressed through canvas, with a mixture of 1 part potassium bichromate, 3 parts hydrochloric acid, and 100 to 150 parts of water. After ten or fifteen minutes, the emulsion is thoroughly washed in plenty of water. The sensitiveness is slightly diminished by such treatment, but may be increased again by the addition of a few drops of ammonia.

(d). Fog is apt to ensue when plates take longer than from three to six days to dry. The upper part of the film remains clear. but a large round spot on the under side of the film shows the part which has been the last to dry. As a remedy against very slow drying, Haack recommends sprinkling the drying-room with carbolic acid. Plates which have been already coated and give fog are more difficult to restore than the solid emulsion They may be laid in the above bichromate mixture, and then

thoroughly washed and dried. Another good plan is to immerse for ten minutes in a solution of 10 parts ferri-cyanide of potassium, 10 parts bromide of potassium, and 100 parts water, and to wash afterwards for some hours.

(*e*). If the plates have been dried at too high a temperature, they are apt to fog during development.

(*f*). Plates which have been kept for a long time in a damp place are inclined to fog and lose their sensitiveness.

(*g*). Lastly, wrapping plates up in unsuitable material, such as paper containing printed matter, various kinds of coloured paper, tin-foil, &c., induces fog, and gives rise to marks, causing an abnormal reduction of silver under the action of the developer.

13. *Red Fog* occurs when an emulsion contains an excess of silver, but this defect is rarely met with in commercial plates. According to Chardon, this phenomenon occurs when an emulsion is prepared with excess of soluble bromide by pouring the bromised gelatine into the silver nitrate instead of *vice versa* An emulsion formed in this way, however, does not give red fog, according to Abney, when developed with ferrous oxalate.[1]

14. *Yellow Fog* occurs during development with alkaline pyrogallic. It is due to the employment either of inferior pyrogallic acid, too concentrated a solution, or the excessive addition of ammonia. An old, discoloured developer will also give the same defect. A negative which has been discoloured in this way may be treated, after fixing, with a saturated solution of alum containing hydrochloric acid ½ per cent. to 1 per cent., or with a weak solution of potassium cyanide. The acid should be washed off as quickly as possible, otherwise the film is likely to blister. If ferrous oxalate be used as a developer, and not thoroughly washed off before fixing, it turns the fixing solution yellow, and the negative becomes discoloured.

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[1] "Practical Working of the Gelatine Emulsion Process" (Piper and Carter, London).

15. *Green Fog* may be due to various causes. Abney mentions a kind of green fog, which is di-chroic, being green by reflected light, and pink by transmitted light.[1] This kind of discolouration may sometimes be removed by soaking the film in a solution of potassium bichromate, but hydrogen peroxide will be found more effectual.

16. *A White Opalescent Veil* often occurs in developing with ferrous oxalate. This makes its appearance when plates are washed in water containing lime. The deposit can be removed with weak hydrochloric acid, but it is of no consequence, as it is quite transparent, and cannot be detected after the negative is varnished.

17. *The Plates, when Developed with Ferrous Oxalate, become covered with a Yellow Deposit.*—This defect occurs when too large a proportion of ferrous sulphate is used in working with the mixed developers. If the acid potassium salt be employed, or if the neutral salt has been rendered acid, the deposit is thrown down in large quantities.[2]

18. *Clear, Undefined Spots and Marks*, visible after fixing, show that the gelatine employed contains grease. They do not make their appearance when the emulsion has been treated with ammonia, and subsequently washed.

Small Pinholes are caused by particles of dust adhering to the plate, which prevent the light, as well as the developer, from acting. Plates should be dusted over before exposure with a broad camel's hair brush.

19. *White Marks or Round Spots* with a sharp outline, which have a glossy appearance after fixing, are caused by air-bubbles adhering to the plate during development. They may be avoided by rinsing the plate in water previous to development, or by keeping the developer in gentle motion.

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[1] "Practical Working of the Gelatine Emulsion Process" (Piper and Carter, London).

[2] See my remarks on "Turbidity in the Ferrous Oxalate Developer," *Photo. News*, 1880, xxiv., 281.

20. *Opaque Spots* of a more or less irregular outline are due to a reduction of silver caused by specks of dust dropping on the plate during coating or drying. Gelatine plates which have been soaked in alcohol to accelerate the drying frequently show these opaque spots.

21. *Irregular Zig-zag Lines* are caused when stoppages have occurred in the flow of the developer. Soaking the plates for a short time in water assists the flow of the developer.

22. *The Image is Foggy.*—This is generally due to over-exposure, or to the development having been forced by addition of ammonia, without a corresponding amount of potassium bromide.

23. *The Picture is Harmonious, but Wanting in Density*, when too weak a developer has been employed. An increase in the strength of the developer will always be found a remedy when the emulsion itself is in fault. This defect is more apparent when the emulsion contains iodide of silver, nitric acid, or potassium cyanide, than when bromide of silver alone is present. It may often be due to the films being too thin, or the emulsion being too poor in silver.

24. *The Picture is Hard, and Wanting in Detail.*—This is generally due to under-exposure, to want of sufficient ammonia in the developer, or to the employment of too much bromide of potassium. Under-exposure is difficult to remedy in the case of ferrous oxalate development, unless the reserve developer be resorted to. The defect may lie in the emulsion itself being insensitive, or it may contain too much soluble bromide, and have been very indifferently washed. Such an emulsion requires a powerful alkaline developer, as ferrous oxalate is of very little use under the circumstances.

25. *The Negative is full of Detail, but too Dense.*—When the developer has been allowed to act on the plate too long, the density may be reduced by soaking the plate, after fixing, in a weak

solution of perchloride of iron (1-50 to 1-100). When the density is sufficiently reduced, the plate should be placed in the fixing solution, and, if necessary, the operation can be repeated. 1 per cent. or 2 per cent. solution of potassium cyanide is effective, but is apt to attack the half-tones, and increase the contrast. Burgess[1] recommends soaking the negative, after fixing, in a (1-60) solution of chloride of gold, and, after the yellow colour which it gives to the negative has reached through to the back of the plate, the latter should be again placed in the fixing solution to dissolve off the chloride of silver formed on the film.

26. *The Negative Exhibits a Coarse Grain.*—This is due to defects in preparing the emulsion. The solution of silver has been too concentrated, the emulsion has been cooked too long, too muc ammonia has been added, or the proportion of silver in the emulsion has been too large. It is impossible to remedy this defect.

27. *The High-Lights are Surrounded by a Halo.*—This is sometimes due to a defect in the lens; but it generally occurs from reflection of light from the back of the plate. This defect is not apparent when the films are thick, or when the plates are backed. The proposal to colour the emulsion itself is impracticable, as such a process is found to reduce the sensitiveness of the emulsion[2] There is a reflection from the film itself, too, which often causes this halo round the high-lights. Plates which have a matt surface, or which contain iodide, are not liable to this defect.

28. *The Negative becomes Reversed during Development.*—This phenomenon or (so-called) solarization occurs principally when the exposure has been abnormally long. Plates liable to this defect should be developed for as short a time as possible, and with a weak developer. Sometimes this effect of solarization is

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[1] Burgess' "Argentic Gelatino-Bromide Workers' Guide" (Greenwich, 1880, p. 34).

[2] *Photo. News*, 1880, xxiv., 318.

apparent when only an ordinary exposure has been given. If this is so, probably actinic light has reached the plate before exposure. Too much hyposulphite in the developer also reverses the image.

29. *Frilling and Expansion of the Film*, &c., generally attend the use of too soft a sample of gelatine. It may also be due to incipient decomposition of the gelatine, owing to too long cooking, or other causes, or the use of too thick films. The emulsion may also contain gum-arabic, or the plates may have dried irregularly, the part that takes longest to dry being the first to frill.

(*b*). The same thing occurs sometimes during development with pyrogallic acid when too much alkali has been employed.

(*c*). When the developer or the wash-water is too warm.

(*d*). When too strong a solution of hyposulphite of soda has been used.

(*e*). When plates have been treated with dilute acid solutions.

It is often useful to coat the plates with a substratum of water-glass (1·200), or else give an edging with a solution of rubber. The best cure, however, is undoubtedly to soak the plates either before or else after development in a 3 or 5 per cent. solution of alum or chrome alum for a few minutes. Williams recommends a mixture of—Tannin, 18 parts; alum, 18; glycerine, 48; and water, 380.

Chardon recommends soaking the plates in alcohol before development, and in a 50 per cent. solution of alum between development and fixing. It is often advisable, in developing plates which have a tendency to frill, to use double the ordinary proportion of pyrogallic acid, and make up the solution half with water and half with alcohol.

Chrome alum may also be added to the developer in the proportion of ½ to 1½ grammes to every 500 c.c., or the addition of 1 to 3 per cent. alum to the fixing solution may also be recommended.

Abney[1] advises that plates liable to frill should be coated before development with plain collodion, and then be washed until the greasy lines disappear, and the water flows off the plates evenly. The development may then be proceeded with without any fear of frilling.

30. *The Negative takes a Long Time to Fix.*—This occurs equally when the solution is too dilute or too concentrated. The strength of the fixing solution should be regulated to about 1 to 5.

31. *Intensification with Silver Nitrate.*—Red fog is very apt to make its appearance during the process if the intensifier is not kept continually in motion, if it contains too little acid as a restrainer, or when the last trace of hyposulphite of soda has not been removed from the film. Red fog can often be got rid of by treating the plates with a 1 or 2 per cent. solution of hydrochloric acid, or by soaking in a strong solution of common salt. If citric acid be used in excess, it has a solvent action on the film.

32. *Failures during Mercury Intensification.*—The hyposulphite of soda should be thoroughly washed off in all forms of mercury intensification with the exception of Edwards' method, otherwise the treatment with mercury will give a brown stain.

(*b*). The same thing occurs if the bichloride of mercury is not thoroughly washed off before the ammonium sulphide or hyposulphite of soda is flowed over the film.

33. *Failures in Intensifying with Uranium.*—If the fixing solution is not thoroughly washed off, the film turns brownish red on the application of solutions of uranium salts. Any traces of ferrous oxalate left in the film gives rise to a bluish colour.

34. *The Negative becomes Darker after Fixing.*—This defect may generally be traced to intensification. It occurs when plates

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[1] *Photo. News*, 1880, xxiv., 328.

have been intensified with mercury or with silver, and in the latter case, especially if the precaution has been omitted of removing all free silver by replacing the negatives in the fixing solution. The only recourse left is to remove the varnish and attempt to clear the plate.

(*c*). Negatives which have been printed from before varnishing often turn red, owing to the silver in the paper conbining with the gelatine to form red stains. The stains can be removed with dilute potassium cyanide.

35. Negatives have an opalescent appearance when they have not been thoroughly dry before varnishing.

36. *The Plates Fade after Varnishing.*—This is due to intensification, and is often met with in plates which have been intensified with England's or Edwards' methods. The only remedy is to remove the varnish, and try some other method of intensification.

CHAPTER XI.

PRACTICAL NOTES.

1. *The Precipitation of an Unwashed Emulsion by Alcohol* has been recommended by Wratten and Wainwright,[1] as well as by Obernetter, on the ground that, while the gelatine itself is insoluble in alcohol, the bye-products enter into solution. The process is, no doubt, much more rapid than that of long-continued washing; but it must be borne in mind that potassium bromide and potassium nitrate are both very soluble in water, and only slightly so in alcohol. The ammonium salts are far more soluble. There is another inconvenience attaching to the process, in the fact that gelatine which has been precipitated with alcohol takes a long time to dissolve in water.

2. *Drying of Gelatine Plates.*—There is danger of fog if plates take too long a time to dry. From twelve to eighteen hours is about the correct time; if this period is exceeded, a few drops of carbolic acid may be sprinkled over the floor the drying-room. The easiest and the best way to dry plates is to stand them on racks in an ordinary light-tight room. If there is much moisture in the air, calcium chloride or sulphuric acid may be employed to absorb it. If a drying-

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[1] Abney's "Practical Working of the Gelatine Emulsion Process" (London, Piper and Carter, 1880).

cupboard is used, the temperature should be about 27° C. to 30° C.[1]

3. *Drying Plates by means of Alcohol.*—It has often been recommended, as a means of hastening the drying, to soak the plates in alcohol for a few minutes, after which, if stood on edge, they will dry in an hour or two. This method is good enough for drying test-plates; but it is not suitable for general employment. The alcohol soon loses its power of absorbing water, and plates which have been dried in this manner are liable to spots.

4. *Alcoholic Solutions of Gelatine or Gelatine Emulsion.*—In May, 1880, I observed that gelatine warmed with nitric acid was highly soluble in strong alcohol;[2] but as it also becomes soluble in water, it is of no use for preparing plates. According to Herschel, alcohol to which 2 per cent. of aqua-regia has been adde will dissolve under the action of moderate heat any quantity of gelatine. The film is insoluble in water, and takes about twice as long to dry as a collodion emulsion. Ēther and chloroform have the same solvent action. The use of aqua-regia lowers the sensitiveness of the emulsion considerably. According to Vogel,[3] gelatine dissolves in organic acids without precipitating.[4] His new emulsion consists of a dry gelatine emulsion and pyroxyline dissolved in alcohol and acetic acid. An emulsion prepared in this way retains its normal power of setting, and a 10 per cent. aqueous solution of either oxalic, boracic, or succinic acid will readily dissolve under heat half its weight of gelatine, and the solutions admit of dilution with three times their volume of alcohol. An emulsion dissolved in double its bulk of acidu-

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[1] *Year-Book of Photography*, 1878, 85.

[2] *Photo. Corr.*, 1880, xvii., 10.

[3] *Photo. Mitth.*, 1880, xvii., 50.

[4] If a few drops of acetic acid be added to an ordinary gelatine emulsion, the latter will be found to melt more readily, and to set with greater difficulty. The addition of a small quantity of acetic acid tends to prevent the recurrence of small pits in the film, to which a gelatine that sets too rapidly is liable.

lated water, to which three volumes of absolute alcohol are added, can be poured over plates like collodion, and dries in an hour, giving the same sensitiveness and brilliancy as an emulsion dissolved in water.

Konarzewski prepares a collodio-gelatine emulsion by dissolving 1 gramme of pyroxylin in 50 c.c. alcohol at 36°, and 50 c.c. acetic acid, and adding 10 grammes of dry gelatino-bromide emulsion; the whole being dissolved in the water bath. Such an emulsion can be poured over the plate like collodion, and dries much more rapidly than an ordinary aqueous emulsion. If the plates exhibit any tendency to frill during development, a substratum may be used previous to coating. Schlicht prepares an alcoholic solution of gelatine in the following way. He precipitates an aqueous gelatine emulsion with alcohol, and, when dry, he adds 1 part of the emulsion to 1 part acetic acid, allows it to stand for an hour, and then warms it over the water bath, when solution ensues in about five minutes. One part of a normal collodion and acetic acid (1 to 4) is added gradually with constant stirring, thebottle being kept warm during the addition. The emulsion may then be diluted with $\frac{3}{4}$-part of a mixture of alcohol and acetic acid (4 to 1), and filtered. It is a curious fact that such alcoholic gelatine emulsions are not so easily spoilt by an excess of silver nitrate as aqueous emulsions. Such an emulsion may be prepared with excess of silver without exhibiting any signs of red fog if the excess of silver is removed by means of sodium chloride.

Wilde informs me that gelatine swelled in water is soluble in alcohol to which two or three times its bulk of acetic acid, neutralized with ammonia, is added. Such an emulsion, thinned with alcohol, gives a clear picture, and retains its power of setting for a considerable time.

5. *On the Keeping Qualities of Gelatine Plates.*—Camps had a good opportunity of testing this during the sea voyages that he undertook. He found that they remained unaffected by the

severest changes. The preparation of gelatine emulsion is extremely difficult during the summer months, and many firms discontinue supplying plates during the summer time in consequence.

6. *The Illumination of the Dark Room.* Opinions on this subject are very conflicting. Some photographers contend that a deep ruby light is necessary; others are in the habit of using orange glass only. There is no danger in the latter if the plates are protected from its direct action previous to development. Ferrous oxalate, owing to its deep red colour, is very non-actinic, and a plate covered with a good body of solution can be brought out into white light during development. Whaite suggests the idea of colouring the pyrogallic developer with cochineal for the same purpose.[1]

7. *Hyposulphite of Soda in the Developer.* A trace of hyposulphite of soda during development of wet collodion plates is very injurious. In the case of dry gelatine plates and pyrogallic development a small quantity of hyposulphite of soda has no effect; with ferrous oxalate the case is very different. Abney[2] observed that the addition of a few drops of a solution of this substance to ferrous oxalate brought out the detail rapidly, and he considers that its use admits of the exposure being reduced to one-third. If the plates consist of pure bromide, or contain chloride, there is a chance of a reversal of the image. I may mention that in this process, the time the solution should be allowed to act after the addition of the hyposulphite of soda depends on the acidity of the developer. According to Abney, it is best to add the hyposulphite of soda as soon as the developer has impregnated the film. We have succeeded very well with plates consisting of bromide of silver alone, and find that the best proportions are from 2 to 10 drops of a 1-100 solution to every

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[1] *Photo. News*, 1880, xxiv., 299.

[2] *Ibid.*, 567.

2 ounces of developer. Larger quantities are liable to give reversed images.

8. *Restoration of Old Ferrous Oxalate Solution.*—The solution containing the green ferric crystals should be warmed in an earthenware basin, and potassic carbonate added until no further precipitate is given after filtration.[1] A small quantity of the solution may be tested now and then for the purpose. The filtrate contains only a trace of iron, and consists for the most part of pure potassic oxalate containing an excess of potassic carbonate.[2] The solution may be neutralised with oxalic acid, and a further addition of potassium oxalate made if necessary. If there is much potassium bromide present, it can be removed by the addition to every 100 c.c. of solution of 2 or 3 c.c. of an old 1-10 sensitizing bath. The solution may be used in the ordinary way after having been filtered for development. Kohnkes' suggestion of precipitating the iron with soda, instead of potash, is not advisable, as the solvent action of sodium carbonate on ferrous oxalate is much less than that of the potassium or ammonium salts.

9. *Transparencies with Gelatine Plates.*—These can readily be produced by exposing gelatine plates under a negative to a gas flame, and developing either with alkaline pyrogallic or ferrous oxalate. The former gives a brown, and the latter a black tone, which is to be preferred for this class of work. Transparencies can be employed for the reproduction of negatives, but such negatives are never equal in delicacy to the original. A method was given in the PHOTOGRAPHIC NEWS[3] of producing very beautiful transparencies from emulsion films on opal glass, which can be afterwards improved, if necessary, by retouching with a pencil or crayon.

10. *Paper Coated with Gelatine Emulsion* was suggested in

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[1] *Photo. Corr.*, 1880, xvii., 27.

[2] If all the iron cannot be precipitated by potassic carbonate, caustic potash is used.

[3] *Photo. News*, 1880, 318.

1874 by Mawdsley,[1] and can be prepared in much the same way as Warnerke's sensitive tissue. No doubt, it would be useful for landscape photography, but the films will, of course, require stripping after fixing. Ferran and Paul[2] recommend the following method: A good stout description of paper is moistened and stretched on a board. To render it non-absorbent, the paper is varnished on both sides with a solution of 2 grammes of asphaltum in 100 c.c. anhydrous benzine, and exposed to sunshine for an hour to make it insoluble. Either one of the following solutions is then laid on: 50 c.c. ether, 100 c.c. alcohol at 42°, 1 or 2 grammes wax, stearine, or paraffin; or 50 c.c. ether, 2 grammes wax, and 20 grammes vaseline. After the ether and alcohol have evaporated, the emulsion is laid on with the addition of a small quantity of glycerine in order to prevent it from becoming brittle when dry. The negative, after being developed and fixed, is coated with a solution containing 12 per cent. gelatine and 3 per cent. glycerine, and when dry the film can easily be detached. Paper sensitized with gelatine emulsion has been suggested by Swan.[3] Such paper is now being manufactured by Morgan and Co., of Greenwich, and admits of a large number of prints being made in a very short time. The paper is exposed to gas light under a negative, and developed with ferrous oxalate; the resulting tone being a cold grey, somewhat similar to platinotype.

11. *Employment of Gelatine Emulsion for Reproduction of Drawings.*—Gelatine emulsion is quite as well adapted for this class of work, as it is for landscapes or portraiture. The plates should be well exposed, and developed with ferrous oxalate containing a good deal of potassium bromide as a restrainer. If treated in this way they rarely require any after-intensification, but in case such a proceeding is necessary, mercury is the best agent for the purpose. Ammonia emulsion is most suitable.

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[1] *Year-Book of Photography*, 1874, 116.

[2] *Photo. News*, 1880, xxiv., 365.

[3] *Ibid.*, 318.

12. *Reversed Negatives for Collotype Work* can be produced by exposing with the film side inwards, the necessary correction for the thickness of the glass being made after focussing. In developing such plates, special care must be taken about the cleanliness of the solutions employed, otherwise the surface of the film may be fogged over before the picture which is on the inner side is sufficiently developed.

13. *Direct Positives in the Camera.*—Negatives on collodion emulsion may be turned into positives, after development, by soaking in concentrated nitric acid, the reduced silver being thus dissolved away; and the picture then consists of undissolved bromide of silver. The plate should then be briefly exposed to light, and redeveloped, or treated with ammonium sulphide, when a positive image will result. It is impossible to treat gelatine plates with nitric acid, as the latter attacks the film; but we found that it was possible to employ mercuric nitrate for the purpose, without danger to the film. If a well-developed gelatine plate be treated with a strong solution of mercuric nitrate, a positive image quickly appears. The plate is then washed, and flooded with ammonium sulphide. The mercury solution should not be too concentrated, otherwise the film shrinks, and gets hard. Brooks gives a method for the production of direct positives in the camera. A bromide or chlorobromide plate is developed to the full extent until the picture can be seen at the back of the plate. It is then laid in a 1 per cent. to 2 per cent. solution of iodide of potassium in alcohol. For gelatine plates, it is preferable to employ a solution consisting of potassium iodide 1 to 2 parts, potassium bromide 10 parts, and water 100 parts. The original image disappears entirely in this solution, and a picture consisting of iodide of silver on bromide of silver remains. The plate is then washed, and treated with pyrogallic or ferrous oxalate developer, which attacks the bromide, and leaves the iodide of silver unaffected. In the fixing bath, the iodide is dissolved away.

14. *Moonlight Photographs.*—Gelatine plates, owing to their extreme sensitiveness, are available for this purpose. Henderson, Dunmore, and others have obtained pictures in this way; but the subject is of interest only from a scientific point of view.

15. *Portraiture by Artificial Light.*—In England, France, and Belgium, the electric as well as gaslight is made use of in various studios with gelatine plates. The results are highly satisfactory. In using gas, a Wigham or Sugg's burner is employed. Mr. Laws, of Newcastle, makes use of a large burner by Wigham, consisting of sixty-eight jets, giving a total intensity of light of 1,250 candles. Reflectors are used for diffusing the light,[1] and a shade of blue glass interposed to protect the sitter from the heat. The use of this shield increases a possible exposure of seven seconds to eight seconds. For cartes, Mr. Laws gives an exposure of about eight seconds, and for cabinet portraits twelve to fifteen. The use of gas is well worthy of attention by photographers, owing to its economy as compared with the electric light.

16. *On Blurring in Emulsion Plates.*—This defect, which is very familiar in photographing interiors, is common to collodion plates as well as thin emulsion films, owing to their transparency, and the consequent reflection of light from the back of the plate. The best remedy is to back the plate with some dark, non-actinic substance. Dyeing the film has also been suggested; but this has the effect of reducing the sensitiveness considerably. Plates coated with an emulsion containing iodide of silver are less liable to this defect.

17. *Chloride of Silver in Emulsions.*—An addition of chloride to a gelatine emulsion will not be injurious so long as there is an excess of soluble bromide present. Whilst this lasts the chloride of silver, as fast as it is formed, combines with the potassium bromide to form fresh bromide of silver.

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[1] *Year-Book of Photography*, 1880, 86; *Photo. News*, 1880, xxiv., 338.

18. *The Choice of a Bromide in Preparation of Gelatine Emulsion.*—We are limited practically for emulsion work to the bromides of either potassium or ammonium, as, if the salt of a heavier metal, such as zinc, be employed, it either coagulates the gelatine, or affects its setting power. Potassium bromide, owing to its stability, appears more suitable than the hygroscopic ammonium salt,[1] which discolours under the action of light. The potassium bromide may with several methods be neutral or slightly acid, but not alkaline. The same degree of sensitiveness can be obtained with either the potassium or the ammonium salt, and the bye-products have no injurious effect on the gelatine. I have observed, however, that a solution of ammonium bromide, when heated, is readily decomposed into ammonia and hydro-bromic acid. The former, at a temperature of 30° C., goes off in the form of gas, and still more abundantly at a temperature of 100° C.; hydro-bromic acid remains behind, giving a strong acid reaction, which may be very injurious to the emulsion.

19. Nearly every sample of bromide in the market contains a slight trace of chloride. A small quantity, such as half, up to one per cent., is of no consequence so long as an excess of soluble bromide is present. If, however, the bromide and silver nitrate exist exactly in their combining proportions, chloride of silver is formed; and the same result obtains if the silver is in excess.

20. *Printing with Gelatino-Bromide or Gelatino-Chloride of Silver without Development.*—An ordinary gelatino-bromide plate darkens in a few seconds under the action of light, and, if exposed under a negative for some hours, a picture full of detail is obtained, which, however, disappears in the fixing bath. By fuming the plates with carbonate of ammonia, the darkening proceeds much

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[1] See *Photo. News*, 1880, xxiv., 270; "On the Value of Pure Potassium Bromide for Preparing Gelatine Emulsions."

more rapidly, and denser pictures can be obtained. In producing prints by this method an emulsion containing an excess of silver is preferable to one containing an excess of bromide, as the former darkens more rapidly under the action of light. Such plates, if previously fumed with ammonia, can be employed; but a longer exposure must be given than when ordinary albumenized paper is employed.

Gelatino-chloride of silver for printing without development should also contain an excess of silver, and requires an exposure of several hours. The prints are brownish red in colour, and can be toned with gold.

Emulsions prepared with a large excess of silver are not subject to decomposition. By long keeping, however, they are apt to discolour, owing to a reduction of silver.

21. *Testing Gelatine Negatives before Varnishing.*—It is always well to take a print from a gelatine negative before varnishing, in order to judge whether intensification is necessary. This can always be done if the negative is thoroughly dry; otherwise red stains are apt to make their appearance. Mr. England is in the habit of laying a piece of talc between the negative and the albumenized paper to protect the film.[1]

22. *Retouching* can be carried out on gelatine negatives if necessary before varnishing, if a small quantity of turpentine be rubbed over the film in order to give a tooth to the pencil. It is safer, however, to varnish the film first.

23. *Removing the Varnish from Gelatine Negatives.*—This operation is often necessary when varnished negatives require intensification. It can readily be done by soaking the plate in strong spirit or benzine, which dissolves the varnish, and the plate may then be gently wiped clear of the varnish with a tuft of cotton wool.

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[1] *Photo. News*, 1880, xxiv., 100.

24. *Recovery of Silver from Waste Emulsions.*—For this purpose the emulsion may be boiled for a short time with from one-third to one-sixth of its volume of a strong lye of soda or potash and grape sugar.[1] When the mass blackens throughout, owing to the reduction of silver, and becomes fluid, water is added, and the mixture, after being allowed to settle, is decanted. The precipitated silver can be heated, and melted into a globule. This method is also suitable for collodion emulsion. The silver may also be recovered by boiling the emulsion or treating it cold with hydrochloric acid, which decomposes the gelatine, and when the silver has separated to the bottom of the vessel, the liquid may be decanted off. The best method, however, that I am acquainted with, is the following: To every 100 parts of emulsion 10 parts of concentrated sulphuric acid diluted with 100 parts of water are added. The mixture is boiled in an earthenware jar for ten or twenty minutes. The bromide of silver becomes granular, and after the solution has been diluted with an equal bulk of water it settles to the bottom of the vessel. The liquid may then be poured off, and the precipitate thrown on to a filter and allowed to dry. As this operation is unaccompanied by any disagreeable escape of gas, it is preferable to the preceding.

25. *Cleaning off Old Films.*—This is a matter of greater difficulty with gelatine, than with collodion plates. The former may be soaked in a solution of chromic acid, or in a warm solution of soda. The latter decomposes the gelatine, and the films can then be readily detached by washing. The plates should be soaked in a bath of weak hydrochloric acid, to remove any trace of alkali, and then rinsed.

26. *Increasing the Sensitiveness of Gelatino-Bromide Plates by Fuming.*—Plates which have been exposed to the fumes of strong ammonia at ordinary temperatures, immediately before exposure, will develop rapidly either with alkaline pyrogallic, or, after

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[1] *Photo. Notiz.*, 1880, 41.

rinsing, with ferrous oxalate, and give pictures full of detail. This method should be useful in studio work.

27. *Keeping Qualities of Gelatine Plates during the Summer Months, and the Value of Antiseptics.*—It has often been remarked that gelatine emulsion which has been kept for some time becomes fluid; and the value of the bromide of silver becomes ruined for photographic purposes. In order to prevent this process of decomposition, the addition of antiseptics, such as carbolic acid, thymol, salicylic acid, &c., has been recommended. Experience on this point is rather conflicting. Szekely finds that an emulsion treated with thymol or salicylic acid is equally liable to decomposition during the hot weather. On the other hand, we noticed that while an emulsion containing no antiseptic becomes fluid after three days, another in which thymol or salicylic acid was incorporated kept sound for six or eight weeks, so long as it was not subjected to a high temperature. General experience is in favour of the fact that both thymol and carbolic acid are better than salicylic acid for preserving emulsions from decomposition.

28. *The Function of an Excess of Soluble Bromide or Chloride in an Emulsion.*—The fact is familiar that an excess of soluble bromide restrains the attainment of the highest sensitiveness in bromide of silver, and that an emulsion containing a large excess of bromide, if insufficiently washed, is insensitive, and the reverse if thoroughly washed. The same fact obtains in the case of a collodion emulsion. In reference to this, Wetzlar remarked as early as 1827 that chloride of silver in a solution of sodium chloride becomes converted into a double salt, which is affected by light, whether it be in a moist or dry condition. If an emulsion is prepared with a large excess of soluble bromide or chloride, the slightly sensitive double salt is formed, and it is only by thorough washing that it can be decomposed. We may consequently infer from this the necessity of thoroughly washing an emulsion which has been prepared with a large excess of soluble

chloride or bromide. The value of a large excess of soluble bromide or chloride lies in the fact that it restrains any possible decomposition of the gelatine which may arise during the preparation of the emulsion.

29. *The Value of Gelatine in Preventing the Precipitation of Bromide or Chloride of Silver.*—Hecht has described some experiments that he made with a view of determining this point. A solution of silver nitrate was added to a simple solution of a metallic chloride or bromide, as well as to solutions of the same to which gelatine had been added until turbidity in the solution denoted a precipitation of chloride of silver. The results were as follows:—

(*a*). 100 parts of a 1 per cent. solution of sodium chloride at a temperature of 39° C. or 40° C. retained in solution ·00954 parts silver chloride.

(*b*). 100 parts of a 1 per cent. solution of sodium chloride to which 5 per cent. gelatine had been added retained at the same temperature ·05736 parts silver chloride.

(*c*). 100 parts of a 1 per cent. solution potassium bromide retained at a temperature of 39° C. and 40 C. ·01099 parts bromide of silver.

(*d*). 100 parts of the same to which 5 per cent. gelatine had been added retained ·05950 parts bromide of silver.

These experiments indicate that the presence of gelatine retards to a certain extent the formation of the haloid salts of silver. Practically, a solution containing 5 per cent. gelatine retains five times as much as a solution in which no gelatine is present. After the solution has cooled down, and has stood for some time, a small portion of the salt separates out

30.—*On the Gradual Increase of Sensitiveness in Emulsions by Keeping.*—Captain Abney and Mr. England have stated that an emulsion goes on increasing in sensitiveness, and that plates coated from an emulsion which has been kept for fourteen days are twice as sensitive as when the latter is used fresh.[1] In the case of an emulsion made with either gum or gelatine, which contains, in the first instance, the insensitive modification of bromide of silver, no amount of keeping will produce any appreciable increase of sensitiveness. It is only when an emulsion is extremely sensitive at first, that keeping at ordinary temperatures produces any increase of sensitiveness. An emulsion prepared with ammonia gains in sensitiveness very much if it is allowed to stand for twenty-four hours before washing.

31. In order to obtain films of uniform thickness, the best way is to determine how much emulsion is required per square inch of surface in order to give a fairly thick film, and to measure out the necessary amount each time.; in general, 0·04 to 0·06 c.c. suffices per square centimetre.

32. *Relief Exhibited in Gelatine Plates after Fixing.*—An appearance of relief is often observed in gelatine plates after development with ferrous oxalate, and is very apparent in places where strong contrasts of light and shade exist in close proximity. It may be possible to turn this fact to account in various photo-mechanical processes, in the same way that Scamoni employed it with collodion plates.

33. *On the Proper Strength of the Fixing Bath.*—A very strong solution of hyposulphite of soda appears to act very slowly, owing probably to the difficulty with which it penetrates into the film. It will often be sufficient in such a case to flow pure water over the film, when the fixing will proceed rapidly. The correct proportions of the fixing bath are about 1 to 5 or 10. Cyanide of potassium and sulpho-cyanide of ammonium are not to be recommended for fixing gelatine plates. If the fixing solution is too strong it attacks the silver, and leaves a thin, useless picture.

34. *Substrata for Gelatine Plates.*—If an emulsion has a ten

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[1] *Photo. News*, 1880, 567; 1881, 16.

dency to frill, and it is decided not to correct the emulsion itself, the best method is to coat the plates with the following substratum:—1 part of gelatine is dissolved in 300 parts warm water, filtered, and, when cool, 6 parts of a filtered 1·50 solution of chrome alum is added. The plates are washed, and, while still wet, the chrome alum and gelatine solution is flowed off and on. The first coating will mix with the water, and a second coating may be flowed on, and the plate allowed to dry. It is somewhat difficult to flow emulsion over plates prepared in this way. The best way, perhaps, is to place the plates on a levelled support, and to guide the emulsion up to the edges with a strip of glass. A solution of water-glass (sodium silicate) 1-200 may also be employed for the same purpose. A very useful substratum may be prepared by mixing 3 or 4 parts water-glass with 7 or 8 parts albumen, and 8 to 10 drops of water. The plates are washed, and, after draining, are coated with the substratum. They may then be dried, and, before coating, should be again washed and dried. Forrest recommends, in the Photographic Almanack, the following solution. The white of one egg is mixed with 500 grammes of water, to which 30 grammes methylated spirit and 20 drops of carbolic acid have been added. The solution, after filtering, can be kept for months, and has been found a perfect cure against frilling.

35. *The Sensitiveness of Bromide of Silver under the Action of Different Forms of Developers.*—Vogel made some experiments with his new emulsion in reference to the above, and found that, by the use of acid development, customary with wet plates, the emulsion was five times as sensitive as wet collodion, and considerably more so than collodion dry plates prepared with excess of potassium bromide. Ferrous sulphate as a developer did not give a better result than pyrogallic acid. Ordinary collodio-bromide plates are three times as sensitive when treated with a pyrogallic chemical developer, as when treated with the same in the form of a physical developer.

36. *The Use of Alum or Chrome Alum in Emulsions.*—These substances may be added to an emulsion, either to improve its setting power, or to prevent any tendency to frill. The same result can be obtained by placing the plate, after development, and before fixing, into a concentrated solution of alum. The alum bath used after fixing is recommended for hardening the gelatine, as well as to destroy any traces of hyposulphite of soda which may remain in the film. The brown colour often present in a negative after development with alkaline pyrogallic can easily be removed by soaking the plate for a short time in a concentrated solution of alum, to which 1-32 of its volume of hydrochloric acid has been added. Mr. Carroll and Captain Abney claim that a gelatine plate which has been soaked in a concentrated solution of alum can be intensified with silver without difficulty.

37. *Treatment of the Gelatino-Bromide Image as in Carbon Printing.*—Warnerke has found that an image upon gelatino-bromide, developed with pyrogallol, is insoluble in warm water. Such an image may, therefore, be transferred, and further developed, just as if it were upon bichromated pigment tissue. But, as pyrogallic acid hardens the film, the water for developing must be hot, or contain a little alkali; fixed with hyposulphite, the film is more easily dissolved. An image thus treated may also be used for collotypic printing, ammonia applied to the surface before inking assuring clear prints.

Photo. News, 1881.

CHAPTER XII.

ANALYSIS OF PHOTOGRAPHIC GELATINE AND COLLODION EMULSIONS.

Bromide of silver emulsions have been extensively introduced into the market within recent times. These consist to a certain extent of collodion emulsions, but are principally met with in the form of gelatine emulsion, prepared either entirely with bromide of silver, or occasionally with chloride or iodide of silver in addition to the bromide. These productions vary considerably in the amount of silver they contain, in their sensitiveness, and in price. Generally speaking, the value of an emulsion is made to depend on its sensitiveness, and not on the amount of silver it contains; but as the preparation of highly sensitive emulsions is no longer a secret, there seems no reason why any increase of price should be justified on that score.

I.—Gelatine Emulsion.

In conducting an analysis of a gelatine emulsion, I can recommend the following as a simple and satisfactory method:—

1. Gelatine emulsion may be in the form of jelly, pellicle, or dried films on glass or paper.

(*a*). *Determination of the Amount of Silver.*—10 grammes of the fluid gelatine emulsion is diluted with two or three times its volume of water, and digested with an excess of nitric acid over the water bath for a few hours. The bromide of silver sinks to the bottom in a compact mass, and may then be thrown on a filter, washed, heated to a red heat, and weighed. As a check, the bromide of silver may be reduced to metallic silver by means of potassic sodic carbonate, and weighed in this form. Dry gelatine emulsion should be soaked in water, then dissolved, and treated in the same manner as above.

Plates coated with emulsion should be soaked in cold water, and the film detached from the glass by means of a spatula, after which it may be dried and analysed in the manner already described. The weight of the film may easily be arrived at by weighing the glass plate, while the film is still on and after it has been stripped. A determination of the amount of silver by a simple ignition of the film is apt to give false results, owing to the weight of the gelatine ash, as well as that of any of the bye-products of emulsification, which may not have been thoroughly removed by washing.

(*b*). *Determination of the Amount of Bromide of Silver in the Presence of Iodide or Chloride of Silver.*—The presence of iodide of silver in an emulsion may generally be recognised by the deep yellow colour of the emulsion when poured on a plate. The determination of either of these salts can be made by the ordinary method of precipitation by means of nitric acid. It is sufficient as an approximate method to treat the precipitate with ammonium carbonate, which dissolves the chloride of silver without affecting the other salts. The addition of nitric acid to the filtrate will precipitate the silver in the form of silver chloride. The precipitate from the original solution should next be treated with ammonia, which dissolves the bromide of silver; the remaining precipitate consisting of iodide of silver. The percentage composition of the emulsion can now be determined by a careful quantitative analysis.

(*c*). *Determination of the Amount of Gelatine and Water.*—The amount of water present may be estimated by evaporating and drying the emulsion at a temperature of 100° C. The weight of the dried mass after the salts have been separated gives the weight of the gelatine, but its accurate determination is generally superfluous. Gelatine emulsion so dried gives a percentage of water of about 8 or 10 per cent.

(*d*). *Test for foreign salts.*—This point is of special importance with a view of determining whether the alkaline nitrates formed by double decomposition have been thoroughly removed. For this purpose a quantity of the jelly should be squeezed through coarse canvas, and 50 grammes of it macerated with cold water for twelve or fifteen hours. The soluble salts contained in the emulsion become diffused in the water, and can be determined qualitatively, and, if necessary, quantitatively. This method is usually employed when the emulsion has been prepared with potassium or ammonium salts. It may happen sometimes that potassium cyanide has been added with a view of preventing fog. The presence of this substance, however, is easily detected by the smell.

(*e*). *Alcohol* in the proportion of 5 or 10 per cent. is often present in an emulsion. It can be recognized by the smell of ether given off when the emulsion is treated with sulphuric acid, and the quantity present can be determined by distillation. The presence of antiseptics, such as carbolic acid and thymol, can be detected by their smell when the emulsion is digested with sulphuric acid. Salicylic acid may be tested for by adding three or four volumes of alcohol to the emulsion when dissolved in warm water, evaporating the filtrate, and after extracting the residue with ether, a dilute solution of ferric chloride may be added. A violet colour, unchanged by the addition of acetic acid, denotes the presence of salicylic acid.

(*f*). *An excess of silver nitrate* is rarely found in gelatine emulsions, as employed for negative work in the camera. Gelatino-chloride of silver used for printing purposes without development usually contains a large excess of silver nitrate. The presence of the latter is at once proved by the red colour produced when a neutral solution of potassium chromate is added. The percentage can be determined by dissolving the emulsion in warm water, and treating it with a solution of sodium chloride; or the emulsion may be treated with nitric acid, filtered, and the filtrate tested for silver nitrate by the ordinary analytical methods.

II.—COLLODION EMULSION.

Collodion emulsions are rarely met with now-a-days. They can generally be recognized by the smell of ether, as it is very exceptional that a collodion emulsion is dissolved in any other vehicle than a mixture of ether and alcohol.

(*a*). *Determination of the amount of silver present.*—It is not advisable to heat the emulsion to redness for this purpose, as the pyroxyline goes off in a slight explosion, and some of the silver becomes thereby lost; but it is easy enough to reduce the emulsion to ashes if the following artifice be resorted to. A portion of the emulsion (about 1 gramme) is dried, weighed, and moistened with concentrated nitric acid in a large porcelain dish, which is then heated until the mass becomes red hot. The pyroxyline under this treatment loses its tendency to explode. Any bromide, iodide, or chloride of silver becomes decomposed by this operation, and the ash can be weighed, and the corresponding amount of silver determined. It is more correct, however, to reduce the bromide of silver to the metallic state by treating with sodic potassic carbonate, and to weigh the amount of silver produced.

(*b*). *The determination of bromide of silver*, when it exists in the presence of iodide or chloride of silver, is less easy in the case of collodion emulsion, than in the case of gelatine emulsion. The simplest way is to reduce the emulsion to ashes in the manner already described, and to heat the ash with potassic or sodic carbonate, whereby metallic silver and sodium bromide are formed. The mass is then lixiviated with water, and the bromide, iodide, or chloride salts remaining in solution can be separated in the manner already suggested. The most accurate results can be obtained in the following manner. The emulsion is freed from ether and alcohol, and warmed for a considerable time with a large excess of nitric acid sp. gr. 1·4. The pyroxylin becomes dissolved, and the silver sinks to the bottom of the vessel, and can be washed and examined.

(*c*). *Determination of the solvent.*—The solvents such as ether and alcohol can be separated from the emulsion by distillation.

(*d*). *Testing for an excess of silver nitrate, soluble bromide or chloride.*—Collodio-chloride emulsion, when used for printing without development, and collodio-bromide emulsions generally, contain an excess of silver nitrate. The existence of silver nitrate may easily be ascertained by treating a small quantity of the emulsion with water, and testing the resulting filtrate with hydrochloric acid or potassium chromate.

In a similar manner bromide or chloro-bromide emulsions may be tested for excess of soluble bromide or chloride, although, if the emulsion be thoroughly washed, it should only contain a trace of these salts.

It sometimes happens, and especially in French emulsions, that an excess of a soluble chloride is present, such as potassium, sodium, or copper chloride. The presence of any of these salts can be detected in the filtrate by the method of precipitating the emulsion by means of water. An addition of soluble chloride is often made to an emulsion prepared with excess of silver with a view of removing the latter, and the consequence is that a small quantity of chloride remains in the emulsion.

(*e*). *Testing for the presence of a preservative or sensitizer.*—Collodio-bromide emulsions very frequently contain some organic substance capable of absorbing bromine, and added with a view of increasing the sensitiveness.[1] The substances most frequently added to an emulsion or poured over the plates after they are coated are:—Tannin, gallic acid, pyrogallic acid, decoctions of tea and coffee, morphine, cinchonine, grape sugar, albumen, glycerine, gum, and many others. Mixtures of some of these substances are also often used, as well as small quantities of organic acids, such as citric or acetic. Collodio-chloride of silver emulsions[2] used for the production of transparencies often contain large quantities of organic acids.

(*f*). It is important to observe that the physical character of a collodion emulsion offers some clue to its method of preparation. An emulsion which has been precipitated in cold water appears when dry in the shape of light porous flakes, easily crushed; while that which has been precipitated in hot water is somewhat similar, but much more compact. When the emulsion has been poured into thin pellicles and washed, it gives hard, brittle lumps, which rattle when shaken together.

III.—COLLODIO-GELATINE EMULSION.

This preparation, which has recently been successfully prepared and commercially introduced, consists of a mixture of collodion and gelatine. Collodion pyroxylin and gelatine emulsion are dissolved in a mixture of acetic acid and alcohol. The solution becomes gelatinous at 15° C. or 20° C., and can be rendered fluid by warming. The pyroxlin and emulsion may also be dissolved

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[1] Bromide of silver emulsions prepared with an excess of silver nitrate, and treated with organic reducing agents, decompose after long keeping, and become, in consequence, useless for photographic purposes.

[2] Such emulsions, owing to their being unwashed, contain large proportions of soluble bye-products. The chlorides employed are the magnesium, calcium, and strontium salts principally: in some exceptional cases the cinchonine salt is also used.

in acetic acid and alcohol, or by previously digesting the gelatine with nitric acid or aqua-regia; its constitution becoming so altered as to admit of its becoming soluble in alcohol.

To analyse such an emulsion, it is treated with an excess of water, which precipitates the pyroxylin together with the bromide of silver. These are collected, dried at a temperature of 100° C., and weighed, then carefully ignited and weighed again. The difference in weight represents the amount of pyroxylin originally present. The aqueous filtrate contains gelatine, the weight of which can be determined by evaporation. The amount of acetic acid can be determined titrimetrically, by diluting another portion of the emulsion with water; and the alcohol can be estimated by distillation after neutralization of the volatile acids. I append the following as the result of the analysis of an emulsion similar to Dr. Vogel's patented emulsion :—

Bromide of silver	5·08
Pyroxylin	1·10
Gelatine	5·38
Alcohol	30·92
Acetic acid...	44·11
Water and loss in analysis	13·41

The amount of bromide of silver was determined by igniting the precipitate thrown down after diluting the collodio-bromide emulsion with water. As a check on the weight of the bromide of silver, the latter was reduced to metallic silver by heating with ammonium carbonate, and indicated a percentage of 5·06.

ERRATA.

Page 1, last line, for "ammonium, chloride, and nitrate," read "ammonium-chloride," &c.

Page 4, third line, for "H. Russell in 1867," read "Berkeley in 1877."

Page 58, fourteenth line, for "Herack" read "Haack."

Page 55, eighth line, for "bromide" read "iodide"

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