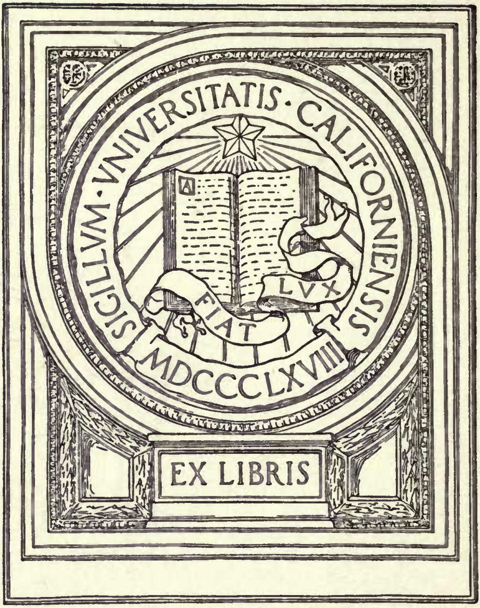
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CHEMISTRY FOR
PHOTOGRAPHERS

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FOR
PHOTOGRAPHERS

By

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TO MY WIFE

As a Souvenir of the Many Photographic Excursions
We Have Enjoyed Together

THIS BOOK
IS
AFFECTIONATELY DEDICATED

PREFACE

THE purpose of the following pages is two-fold. First, the chemical principles whose application forms the foundation of the photographic art are set forth in a manner which it is thought will prove both intelligible and interesting. In order to fix these principles in the reader's mind and at the same time to aid him in the acquisition of a better chemical technique, the subject matter has been so arranged as to permit the introduction of a series of illustrative experiments.

Second, without in any way interfering with the foregoing intent, it has been possible to add very materially to the practical value of the book by incorporating much useful chemical and photographic information in the way of solubilities, formulas, etc. This information has been so simplified and tabulated as to make it exceptionally convenient for reference purposes.

To make special acknowledgment of each of the authorities, chemical and photographic, which must be consulted in the preparation of such a volume as the present one would be both cumbersome and superfluous. The literature of the subject, technical as well as popular, has been freely utilized, and the author would here express his indebtedness to all the writers and investigators whose work has been of so much assistance, but whose names it is impossible to enumerate.

The author's thanks are particularly due to Mr. Lorenzo Whiting of Pasadena, California, who has carefully performed and checked most of the formal experiments included in the text.

In committing this little book to the reader's hands the author sincerely hopes that it will be found helpful, not alone in the saving of time and materials which must come from a better understanding of the processes of photography, but also in an augmenting of the amateur's interest and pleasure in a delightful avocation.

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Chemistry for Photographers

CHAPTER I

INTRODUCTORY

THE two most marked tendencies in the photographic art of today are represented by two different types of workers. One of the types includes those who are the most advanced workers of the day, the pictorialists, whose whole endeavors are being earnestly directed toward the expression of ideas through the medium of photographic processes suitably controlled. The other type comprises the scientific workers, interested primarily in the investigation of the chemical, physical, and physico-chemical principles upon which the science, if we may call it such, of photography rests. Both of these classes have already made their indelible impress upon the art, the former largely in the extreme evolution of the colloid-dichromate methods by which the pictorialists are able with the greatest freedom to give play to their artistic feelings in their prints. The influence of the latter has been felt, not only in the improvement of manufacturing processes and products, but in the revision of our ideas upon the subject of development as a whole, and in the attempt at standardization of many methods.

These two types appear to be at the extremes of photography, the pictorialists, on the one hand, subordinating the scientific and the mechanical as much as possible and laying stress upon the purely artistic, and the scientific workers giving practically the whole of their attention to improving the quality and increasing the accuracy of delineation of the photographic records in which they are interested. Between these two rather widely separated groups are the great body of amateurs and a large proportion of professionals, most of whose photographic operations are still carried on by rule-of-thumb methods. Nevertheless, the numbers of enthusiastic amateurs who go snapshotting more or less at random about the country testify amply to the fascinating power of photography even when its processes are empirically worked. Doubtless it is from watching the wonderful succession of changes through which their picture goes as it passes from one solution to another, together with the certainty, greater or less according to their skill, of being able to produce in the event a particularly desired result, that for most amateurs a great part of the pleasure in their craft comes. It is with the purpose of helping to increase and extend this fascination and pleasure, by adding a clearer understanding of what goes on in these processes, that we shall proceed, in the succeeding chapters, to discuss the chemical principles which underlie them.

The endeavor will be made, with what success the reader must judge for himself, to describe and explain in an elementary way the manner in which chemical reactions, delicate and, very many of them, exceedingly intricate, are so controlled as to yield both the photographs of the everyday amateur and the works of art of the skilled pictorialist. The author has been led to make this attempt because of the conviction, impressing itself more and more strongly upon his mind with the growth of his own experience and the extension of his reading and study in photographic matters, that the admittedly low standards of most amateur and a large proportion of professional work are due mainly to two causes. The first of these is the failure to understand the chemistry of photographic processes, and the second, the lack of appreciation of the principles of composition, perspective, and those qualities which go to make a picture. Now, of course, not every photograph needs to be a "picture," and no one can rightfully quarrel with the amateur who prefers to make photographically a purely literal record of his experiences, whether everyday or vacation. However much the advanced pictorialist may pity such an amateur, there is a great deal of interest and charm in the making of straight record photographs. But the photographers who make them ought, for the sake of their friends if not for their own, to try to make them as perfect as possible. This is the reason why, of the two causes just mentioned, the chemical was placed before the artistic; for it must be from the teeming ranks of the aspiring amateur "straight" photographers that the majority of "advanced" and "pictorial" workers are recruited. The first essential, therefore, is to inculcate as widely as possible a more intelligent conception of the chemical foundations upon which photography rests, in order that the average photographer may better understand his medium, improve his practice, and thereby perfect his results.

There has in the past been prevalent among more or less advanced workers the fear that their art might become too mechanical, and for this reason there seems to have been almost a prejudice against putting the formulas for developing and other solutions into reasonable chemical shape. Such photographers, for example, in recommending a recipe for developer, would suggest adding "a pinch of pyro" to a specified mixture of alkali and sulphite, or "as much pyro as will go on the point of a penknife." At the present time there does indeed appear to be a deal of the mechanical and automatic in photography. It has come about, however, not from the standardizing of formulas and manipulations, but from the output of numerous, and it must be admitted extremely convenient, prepared powders and solutions, most of which need the addition of nothing but water. The user, therefore, is generally ignorant not alone of the concentrations of the active agents in his solutions, but often of the very identity of their constituents. He performs certain manipulations according to the printed directions, but naturally can comprehend little of their real import. The author hopes in the following chapters to aid in changing this state of things, by helping the worker to understand, to take an example, that when an exposed plate is developed there is an equivalence between the quantity of silver reduced and the amount of developing agent oxidized; that it is this reaction which uses up the developing agent, aside from its spontaneous oxidation by the air; and that because by these oxidations the concentration of the reducing agent is diminished, it is better, for the sake of clean, uniform negatives, to use a given small portion of the developer solution but once, and then to throw it away, rather than to use it over and over again until it is exhausted. The quantities of substance of which photographic images are composed are so minute that the concentrations of the active agents with which these images are treated have to be controlled with considerable care. It is one of the axioms of physical science that the same causes always operate to produce the same effects. Since photography depends so largely upon the operation of physical and chemical laws, it ought to be plain that obedience to them is the key to success, represented by well-executed, permanent, and attractive prints.

As all physical science rests upon an experimental basis, and especially since a much better idea of the laws and phenomena of a science can be had by actually performing for oneself even the simplest of experiments than by any amount of reading about them, the author has incorporated with the text of this discussion a set of selected experiments intended to illustrate the principles which are developed. He emphatically recommends that the reader perform every one of these experiments in course. No elaborate apparatus is needed for them, and the chemicals are those which are most commonly used by photographers. Neither is any special equipment necessary, but either the kitchen sink or the amateur's ordinary darkroom will serve quite as well as though it were the most fully equipped chemical laboratory. In working them out it will be found helpful to determine first of all exactly what is intended to be illustrated in each case, that is, the object of the experiment. Then pay close attention to everything that goes on as the reaction progresses. There is nothing too insignificant to be noted down. A class of young chemistry students once discovered that in the very simple operation of boiling a little water in a test tube there are some twenty-five different phenomena which can be observed. It is in this way that one's powers of observation are cultivated, and that is an end that is very well worth while in itself. And, finally, all the facts which are observed ought to be written down, with such inferences as can be drawn from them. By this means they will be the better fixed in mind and can easily be referred to later, if necessary, without the experiment having to be repeated. The habitual use of a notebook in which are recorded facts, observations, comments, *etc.*, is a good custom for anyone to adopt, and it is particularly so for the photographer, who ought to make a practice of recording the data of all his exposures. While the author feels that his work will be of the most help if his readers will conduct the experiments as they are described and along the lines just suggested, nevertheless he has so arranged the directions for doing them that no one need be deterred from studying the book by inability to perform some or all of them.

So much has been written upon the darkroom, *per se*, and upon its plan and arrangement that we need spend no time in discussing it here. Besides, almost every photographer has his own special ideas about it, or has his own special conditions to contend with in its location and construction. It will be sufficient and quite satisfactory to assume that he has devised an arrangement which suits his convenience as well as possible. And beyond this we need not go, since we have already remarked that the place in which the experimental work is done is of little consequence beside the manner in which it is done. But there are certain simple items of apparatus which, while often found in the photographer's workroom, we had best enumerate for the sake of any one who may not have them at hand. The first, and indispensable, is a balance and set of weights. The balance may well be the regular photographic scales, or either the very cheap hand scales with horn pans or the slightly more expensive "coarse weighing" balance supplied by the dealers in laboratory apparatus. It need not cost more than $3.00 or $3.50 for the one last mentioned, which must be capable of weighing to 0.05 gram at least and up to 100 grams. With the photographic scales there usually is furnished a set of grain weights, but they will not be useful in connection with the present work. Curiously enough, these sets of weights are commonly a mixture of avoirdupois and apothecary weights. This ought to be sufficient comment upon the system. The set required runs from a 50-gram piece down to 0.05 gram and costs not more than a dollar. There is much satisfaction in the use of a good, substantial balance which does not easily get out of order, and it is excellent advice to get the best that can be afforded. But there is no need to exceed the specifications given for capacity and sensitiveness. In lieu of means for weighing out the chemicals for the experiments himself, the worker who has no balance can probably persuade some druggist friend to weigh them out for him. Besides the ordinary darkroom equipment of trays, tanks for developing and fixing, and glass-stoppered bottles for solutions, *etc.*, it will be most convenient to have a few items of glassware. These are obtainable from any dealer in laboratory apparatus and for a very moderate outlay. The list of articles will be found in the appendix at the back of the book, where is also included a list of the chemicals needed in the experiments.

The subject of photography, as we have intimated, is a very wide one. Viewed from whatever direction, in its enormously varied applications, in its purely scientific investigations, and in its adaptation to the uses of the amateur, its development has been little short of marvelous. What further progress is still to be made only the future can tell. And yet, from the photomicrographs of the biologist to the stellar photographs and the spectroheliograms of the astronomer, from the record photography of the amateur to the best work of the great pictorialists, the whole structure of the art is based on the one simple fact of the remarkable action of light upon certain chemical compounds. The succeeding chapters will treat of this action and of these compounds in a way that the author hopes may be found not only intelligible and interesting but instructive and helpful.

CHAPTER II

CHEMICAL REACTION

ONE of the most general observations which can be made about the world in which we live is that nothing remains unchanged for any considerable period of time. The appearance of a landscape under bright sunshine is continually subject to change as the shadows shift with the altering position of the sun. The study of these variations in the same view forms a most useful exercise for the photographer who is interested in landscape work. Beneath a clouded sky the view presents a totally different aspect from any of these appearances. If we pass to a consideration of the sky on such a cloudy, gray day, we shall see that even the clouds are not uniform. There are lighter and darker grays. By fixing the attention upon a single patch of gray cloud, we find that the quality of grayness is changing in both tone and texture.

Let us walk down beside the clear pool which, with its elliptical outline and its reflections, forms such an attractive feature in our imaginary landscape. Whether the air is still or whether a breeze ripples the water; whether we see in its mirror-like surface the clear blue of the sky or the rolling masses of a dazzling white thunderhead, surely, we may think, here is a body that is not changing. Water is water; the observed changes are external to the body itself and are only appearances. The physicist comes along with a little delicate apparatus and shows us that the vapor of water is continually rising from the surface of the pool. And more than this, by certain experimental and mathematical considerations he can also prove to us that water vapor is at the same time condensing from the air into the pool. Here then it seems is a different sort of change from the changes in the appearance of things of which we have been speaking. And yet it is only seemingly different because invisible to the eye. The physicist will tell us that all these changes are physical changes because the identity of the bodies concerned has not in any case been really affected. For example, whether water be liquid water or vapor of water, its identity is the same; only its condition has suffered a change.

Let us now go around the pool to the big tree on the other side. We know that its beautiful green leaves, which came out of the winter buds early in spring, will be changed into an autumn glory in the coming fall. But for the time being they are just green leaves, and cannot it be said that they are unchanged, temporarily at least? The answer now comes from the chemist. By the very simple device of putting a leaf into a tube full of water and standing it in sunlight, he can show that all the while the sun is shining upon it the leaf is busily engaged in consuming one of the constituents of the air, namely, carbon dioxide, retaining within itself the carbon with which to feed the rest of the plant, and breathing out the oxygen. That the bubble of gas collected at the top of the tube really is oxygen can be proved by bringing into it the end of a glowing splinter of wood, whereupon the spark will burn much more brightly than in the air.

So from the chemist we learn that in this operation of the green leaf under the influence of light there are three bodies concerned. First, there is carbon dioxide, a colorless gas in which a glowing splinter is extinguished; second, oxygen, also a colorless gas, but a supporter of combustion; and third, the carbon. Dismissing the leaf from further consideration with the remark that it is able to assimilate this carbon in such a way as to store it up in the woody structure of the plant, we may note that carbon is ordinarily a black solid substance, quite different in every way from either of the other two. Stating the proposition again and in another form, we may say that it is possible to take the colorless gas, carbon dioxide, and to get from it another colorless gas, oxygen, and black solid carbon. This would be plainly a different kind of change from the vaporization of liquid water into water vapor or the condensation of water vapor into liquid water, which, as we have seen, are physical changes because the identity of the water is unaffected. It is, indeed, a chemical change, for the identity of the carbon dioxide is lost, and two new bodies whose identity is different are obtained. Thus we may define as chemical changes all those changes by which the identity of the bodies concerned is altered.

By much patient investigation chemists have proved that all the many thousands of different kinds of bodies are various combinations made up from only about eighty really different kinds of matter. These eighty substances are known as the chemical elements, because none of them has so far ever been separated into anything simpler. When any two or more of the elements combine in such a manner as to form a definite substance, a chemical change occurs because there is a change of identity. This change is called a chemical reaction, or simply a reaction. Thus the chemical change already considered, that of the carbon dioxide into carbon and oxygen, is a reaction. It is possible to state reactions very simply in terms of the substances involved and in the form of equations, and for the sake of clearness, as well as for another reason which will presently be shown, it is very useful to do so. For example, we may write the reaction we have been discussing thus:

Carbon dioxide = Oxygen + Carbon

Now, in order to discover just how useful this way of writing reactions may be, and especially to learn what they really mean, let us perform and then consider a carefully conducted chemical experiment. In performing this experiment, keep the eyes and face away, just as though you were setting off flash powder.

Experiment 1. Upon a small piece of thin white porcelain place a very little powdered magnesium taken from a box of flashlight powder. Spread the magnesium out in a thin layer, and, supporting the porcelain suitably, cautiously apply heat to its lower side with an alcohol lamp or a gas burner, until all action ceases. Then remove the source of heat, let the porcelain cool, and examine the substance which it now holds.

If we have made any adequate use of our powers of observation, we shall have noted in the first place that the magnesium, which by the way is one of the elements, is a silvery white substance, noticeably light in weight, or, as we should rather put it, of low density, and metallic looking. In the second place, when it was heated sufficiently it began to melt; but in the third, before very much of it was able to fuse, it took fire and gave out a bright light together with a puff of white smoke. And, finally, after cooling it, we have found upon the porcelain, in place of the original magnesium, a white powder which bears no resemblance at all to the material with which we started. What is it that has happened? Generally we shall find that restating such a proposition will help to make it clearer. We have taken the metallic element, magnesium, and added heat to it in the presence of the air; and have thereby obtained more heat, a bright light, and some white powder. This white powder, a chemical analysis would tell us, contains nothing but magnesium and oxygen, and the chemist therefore calls it magnesium oxide. No matter how many times we may repeat this experiment, we shall always find at its conclusion the same sort of residue, namely, magnesium oxide. And, furthermore, if we had more experience and much more elaborate apparatus, we might weigh the magnesium beforehand and then, performing the experiment with very great care, weigh the magnesium oxide produced. If we were to do this a number of times with different amounts of magnesium, we should find that, allowing properly for what are called the experimental errors, the weights of magnesium oxide produced would all be in the same proportion to the weights of magnesium taken to start with, and this ratio would be 40.32 of magnesium oxide to 16 of oxygen. In other words, when a definite weight of magnesium is heated in the air, it takes from the air a definite weight of oxygen and forms a definite weight of magnesium oxide. So, then, we may write this reaction as an equation:

$$\begin{aligned}&\text{Magnesium } (24.32) + \text{Oxygen } (16) + \text{Heat}\\ &\qquad = \text{Magnesium oxide } (40.32) + \text{Heat} + \text{Light}\end{aligned}$$

By using other elements and substances than magnesium and oxygen, it is found that the same rule of definite parts by weight holds true for all, although, of course, the numerical ratios are different. Therefore by our experiment, together with the considerations just developed, it has been shown, first, that each definite chemical compound always consists of the same elements combined in the same proportions; and, second, that when two substances combine chemically they always combine according to definite proportions by weight. These are two fundamental chemical laws, the law of constancy of composition and the law of definite proportions, and they are of great importance because from these known ratios and proportions there can always easily be calculated, not only the percentage composition of substances, but also either the amounts of combining substances to use in order to get a particular quantity of the compound, or what quantity of a compound can be made from given amounts of its constituents. Thus, from our equation and the ratios given, the proportion of magnesium in magnesium oxide is $24.32 \div 40.32$; of oxygen is $16 \div 40.32$; and to make ten pounds of magnesium oxide will require the burning of $10 \times 24.32 \div 40.32$ pounds of magnesium.

We will next make an experiment by applying heat to a compound.

Experiment 2. Crush to a fine powder a few small crystals of silver nitrate, make a little pile of the powder upon a clean piece of thin white porcelain, and heat it carefully from below. Continue to heat until all fuming has ceased and the residue is bright and silvery. Cool and examine this residue.

Here we start with a white powder, and by heating it convert it to a bright metal, evidently silver. In the course of the heating, brown fumes are given off, the material is hot simply on account of the heat we are applying to it, and no light is given out. So this reaction appears to be in every way the reverse of that in the first experiment. Before we can write out an equation, it is necessary to know positively whether the silver residue and the brown smoke, which is an oxide of nitrogen, are the only products of the reaction. By putting a little silver nitrate in the bottom of a glass tube, closed at one end and open at the other, and heating it, and presently applying a glowing splinter of wood at the tube's mouth, we can show that oxygen is also given off. Finally, by carefully preparing pure silver nitrate in the first place and weighing it and then weighing the residue of silver, we should find that, just as there is a definite ratio between magnesium and magnesium oxide, so there is a fixed proportion by weight between the silver and the silver nitrate from which it came. This ratio is 169.89 silver nitrate to 107.88 silver. We are now in position to write the reaction in the form of an equation if we add that it can be shown by suitable means that fixed proportions of oxygen and of nitrogen oxide are also produced:

Silver nitrate (169.89) + Heat
= Silver (107.88) + Oxygen + Nitrogen oxide

Leaving the further comparison of this reaction with that of Experiment 1 for our later consideration, we will pass at once to two others.

Experiment 3. Measure in a test tube with a small glass graduate 5 cubic centimeters of water. Weigh out upon the balance 0.1 gram of silver nitrate and dissolve it in the water. In a similar manner make another solution in a test tube of 0.3 gram of sodium chloride (common salt) in 10 cubic centimeters of water. Warm the silver nitrate solution, add to it a little of the sodium chloride solution, and shake the tube containing the mixture. Add more of the sodium chloride and shake, and continue thus until it is seen that no more white solid forms upon the addition of a drop or two of sodium chloride solution. If the experiment has been carefully done, the white solid, or "precipitate" as it is called, will collect in little bunches and settle quickly to the bottom of the tube. If not, shake vigorously, and then let the tube stand until all the solid has settled, which should take only a few minutes. Now, remembering that a little of the sodium chloride was added after the white powder ceased to separate from the silver nitrate solution, consider how to free the solid substance from this sodium chloride and any other substance that may be in solution in the water. Suppose that, taking care to disturb as little as possible the solid in the bottom of the tube, we pour off from it all of the liquid we can, and then put 10 cubic centimeters more of fresh water into the tube. Shake the tube, let the powder settle again, and then pour away the water. By sufficiently often repeating this process, which is called "washing by decantation," it is clear that each time we shall leave in the tube only a portion of whatever substances may be in solution, and thus may reduce the amount of them to as small a quantity as we please.

We may test the efficiency of this washing process as follows: Dissolve in 4 or 5 cubic centimeters of water contained in a test tube a small crystal of silver nitrate. Into another clean test tube pour the wash water from the tube containing the original precipitate. Now add to this wash water a few drops only of the new silver nitrate solution. If the wash water still contains an appreciable amount of sodium chloride, a white cloudiness will appear, just as the white precipitate was formed in the first instance. As soon as a portion of wash water shows no perceptible change upon testing with silver nitrate in this way, we may consider the precipitate thoroughly washed.

(NOTE.— It should be remarked here that other soluble chlorides besides the chloride of sodium will also form this white precipitate in a solution of silver nitrate. Since in some localities the natural waters contain appreciable amounts of chlorides in solution, the addition to them of silver nitrate will produce a cloudiness as above described. Thus with such waters it will be impossible thoroughly to wash the precipitate. In these cases distilled water should be employed for this experiment.)

In performing this experiment we shall have observed that in the case of both substances the solid readily dissolved in the water without any other perceptible change; but that a change occurred as soon as the two solutions were mixed; and lastly that after a certain point the addition of sodium chloride failed to show any further change. It might be supposed that the sodium chloride caused the silver nitrate to come out of the solution as silver nitrate, or, *vice versa*, that the sodium chloride was forced out, in which cases the change might be a physical change. But investigation of the white precipitate would show that whereas it contains silver it contains also chlorine; and that it contains nothing besides these two elements. It is thus silver chloride, and therefore the formation of the white precipitate indicated a chemical change. We must next consider what has become of the sodium from the sodium chloride and the nitrate part of the original silver nitrate. If we have in the first instance added but a drop or two more of sodium chloride after the silver chloride stopped precipitating, we could take the solution decanted from this precipitate and boil it down carefully to small bulk in a little dish and set it at one side for a day or so. We should then find that a white solid substance had crystallized out and examination, perhaps with a magnifier, would show that the crystals have a different shape from either sodium chloride or silver nitrate crystals. Also by conducting the experiment quantitatively, adding to a known amount of silver nitrate a definite quantity of sodium chloride in excess, and weighing the silver chloride precipitated, it can easily be proved that besides the silver chloride the only other new substance formed is sodium nitrate. Therefore it should be noted that we have also indicated by the experiment that when silver chloride is formed by interaction of silver nitrate and sodium chloride, exactly the right amount of sodium is involved to form sodium nitrate with the nitrate from the silver compound. There is neither nitrate nor sodium left over, so to speak. Looking at the matter in this way, we may see that any definite quantity of silver nitrate is perfectly matched by some other definite quantity of sodium chloride, because, while there is just enough and no more silver in the one to combine with all the chloride in the other, and form silver chloride, at the same time there are exactly suitable amounts present of sodium and nitrate to form sodium nitrate and have nothing left over. Such amounts of two interacting substances are called equivalent amounts, or simply equivalents. We are now able to write the reaction as an equation:

Silver nitrate (169.89) + Sodium chloride (58.46)
= Silver chloride (143.34) + Sodium nitrate (85.01)

To keep the matter fresh in our minds we will note again that by using the proportions of these numbers, which we now will call the equivalents of the substances, it is possible to calculate from a given weight of any one of the compounds the corresponding weights of all the others.

Experiment 4. Dilute with water a few cubic centimeters of strong hydrochloric acid (muriatic acid) to 25 cubic centimeters, mix thoroughly, and put 20 cubic centimeters of the solution into a small porcelain dish, saving the remainder, 5 cubic centimeters, in a test tube. To 5 cubic centimeters of water contained in another test tube add two or three drops of strong ammonium hydroxide (ammonia water) and mix by shaking. Dip into the smaller portion of diluted hydrochloric acid one end of a strip of red litmus paper, and similarly a strip of blue litmus paper, and observe the effects. In the same way try the action of the diluted ammonium hydroxide upon red and upon blue litmus, and compare these effects with the former. Evidently the litmus can be used to indicate the presence of these substances in solution, and for this reason it is called an "indicator."

To the bulk of the hydrochloric acid solution in the dish add cautiously strong ammonium hydroxide, little by little, stirring after each addition to mix the liquids. Continue this operation until the mixture smells very faintly of ammonia. Try the effect of the solution now upon red litmus, and consider what has happened to the hydrochloric acid in the operation. Leaving the strip of litmus paper in the liquid, cautiously add, a drop or two at a time, some of the diluted hydrochloric acid from the test tube until, upon thorough stirring, the litmus just turns red. Then add with still greater care a very little diluted ammonium hydroxide, continuing thus with one or the other of these dilute solutions until, if possible, red litmus remains red and blue remains blue, or at any rate the color change is very slow. After the removal of all strips of paper, the dish is to be set over a burner in such a way that all the water may be evaporated slowly, the dish at no time being permitted to become hotter than the boiling temperature. Examine the dish for any residue. Boil away a little of each of the dilute solutions separately and see whether any residue is left in either case.

(Note.—If, after all the water has been evaporated, the dish is heated much above the boiling temperature, the experiment will probably be spoiled, since the residue also will be expelled. It is quite likely that both the liquid and the residue may be slightly colored from the litmus, if the strips of paper have been allowed to soak in the dish for any length of time. Keep the litmus out of the solution as much as possible, and the residue will be nearly, if not quite, white at the end of the experiment.)

Remarking that "hydrochloric acid" as supplied is merely a solution of hydrogen chloride in water, and that ammonium hydroxide is likewise a solution of ammonia, both these compounds being gaseous, we may, if we look at the equation which represents the reaction of Experiment 3, perhaps at once venture to write an equation for this reaction, as follows:

Ammonium hydroxide + Hydrogen chloride
= Ammonium chloride + Hydrogen hydroxide

The white residue is therefore ammonium chloride, since hydrogen hydroxide is only a chemical name for water. This reaction is a very remarkable one, in spite of its apparent simplicity. Two clear, colorless liquids, neither one of which upon evaporation leaves any residue, the one smelling strongly of ammonia and the other producing a pungent, stinging sensation in the nostrils, when suitably mixed form a solution which has practically no odor at all, from which a white solid substance is obtained by evaporating the water. It is also to be noted that the two substances, ammonium hydroxide and hydrogen chloride, interact spontaneously and without the intervention of heat, just as did the silver nitrate and sodium chloride of the preceding experiment; that heat is developed by reaction, as could be shown by using stronger solutions of the substances; and, as in the foregoing experiments, that if the quantities of interacting substances and products were measured they would be found in definite proportions to each other. So we will write the equation again in the following form:

Ammonium hydroxide (35.05) + Hydrogen chloride (36.48)
= Ammonium chloride (53.502) + Water (18.016) + Heat

Since, as we have seen, the two odors mutually destroy each other, it is but a step to the inference that the ammonium hydroxide and hydrochloric acid have neutralized each other. Indeed, there is a whole series of substances that possess, like the acid, a sharp, sour taste when sufficiently dilute, are generally powerful, corrosive liquids in concentrated form, and have certain other important properties in common. And there is another series, like the ammonium hydroxide, possessing in dilute solution a soapy taste, generally solids forming more or less caustic solutions. And the members of the first series interact with those of the second series in the same way as the hydrochloric acid and ammonium hydroxide. The first are called acids and the second, bases. The process of their interaction, which is always accompanied by the development of heat, is called neutralization, and the principal product is a "salt" in each case, the other product always being water. So when a given solution contains an excess of acid, or free acid as it is called, if the excess is undesirable it may be readily destroyed by the addition of a sufficient amount of a base, or *vice versa*. Ammonium hydroxide is often used for getting rid of an excess of acid because it is itself volatile, and if an excess of alkali is also not wanted it can be expelled by heating.

In these four experiments we have learned that elements will sometimes unite to form compounds if sufficient heat energy be supplied to them; that compounds may be caused by heat to break apart into the elements of which they consist; and that often when chemical reactions occur there is a development of heat, and sometimes even of light. Sometimes, as in the decomposition of silver nitrate in the second experiment, the reaction does not yield heat, but on the other hand heat disappears, being used up in the progress of the reaction. Thus every chemical reaction is accompanied by an energy change of some sort. Even when, as in the neutralization of a base by an acid, the reaction starts spontaneously, that there is actually a change in the energy conditions is proved by the appearance of heat when the base and acid are mixed. This fact of a relation between energy and chemical reaction is of the greatest importance in very many ways which need not here be discussed. But in the chemistry of photography it is vital, for it is the reaction produced in the photographic emulsion by the energy of light which makes photography possible.

By a comparison of the experiments we may also learn that there are several different types of reactions. When two or more elements or substances are caused to combine, as in the burning of magnesium with oxygen to magnesium oxide, the elements are put together, and the reaction is thus a reaction of synthesis. On the other hand, it is possible, as in the second experiment, to cause compounds to be broken up into their constituents, and then we have reactions of analysis. It is the use of this kind of reaction, whereby the composition of substances is investigated and their percentage composition determined, which constitutes that branch of chemical science known as analytical chemistry. In such reactions as that between silver nitrate and sodium chloride and between hydrochloric acid and ammonium hydroxide, we appear to have compounds picked apart and put together again in a different order. These reactions, in which there is a change of partners so to speak, are reactions of metathesis. But there are still other ways in which reactions may be classified, for example, we have already shown that in Experiment 4 the process of neutralization is illustrated. When the dry substances are mixed together and reaction is brought about either without or with the aid of heat, it is sometimes said that the substances react "in the dry way;" and the reaction may be said to take place "in the wet way" when it occurs between substances that are in solution. The most important kinds of reaction for our discussion, however, are typified in the first two experiments, since it is by means of such reactions as these that the initial work of light upon the photographic plate or film is afterward made effective in the negative (or print) and the result finally modified to suit the requirements of the photographer.

When, as in Experiment 1, oxygen is caused to combine with a substance, that substance is said to be oxidized, and the reaction is called oxidation. The oxygen may come, as in the experiment, from the supply of free oxygen gas in the air, or it may be taken from (or given up by, whichever way we choose to look at it) some other compound, generally one that is rich in oxygen. The substance which furnishes the oxygen is called an oxidizing agent or simply an oxidizer. If we now consider what has happened to the oxidizer, namely that oxygen has been taken away from it, we shall see that this is precisely what has occurred in heating the silver nitrate, viz., oxygen has been removed. This is evidently the reverse process to oxidation, and it is called reduction. The substance, as for instance silver nitrate, from which oxygen is taken is said to be reduced; and that which takes the oxygen is called a reducer. It may now be remarked that a reduction cannot occur without an accompanying and equivalent oxidation, and *vice versa*. The substance which is oxidized need not be an element, it may even already be an oxide. As an example, there is an oxide of lead, litharge, which is capable of being oxidized, forming another oxide of lead, richer in oxygen, lead dioxide, or, as it is sometimes called, lead peroxide. This lead peroxide is a strong oxidizing agent, readily giving up again exactly the amount of oxygen which was required to change it from litharge to peroxide. After the peroxide has been reduced to litharge, the latter can be further reduced to metallic lead, by using still more powerful reducers. Reduction, therefore, may also be conducted in steps, a higher oxide being reduced to a lower, and the lower completely reduced, as to a metal. By an extension of these principles, chemical changes in which no oxygen at all is involved are denominated oxidation and reduction. As an example may be cited the action of a piece of iron, such as a nail, on a boiling solution of the chloride of iron which is called ferric chloride. The solution is originally yellow in color, but the boiling over metallic iron bleaches out the yellow and makes the solution colorless. At the same time a little of the metallic iron is dissolved. By suitable analytical tests it can be shown that the solution now contains chloride of iron and nothing else, but the iron chloride is a different one from the original. If it were taken out of the solution it would be found to be a white powder, whereas the ferric chloride is yellow. The new compound is ferrous chloride, and it is made from the ferric compound by reduction, iron being the reducing agent. It will perhaps be clear at once that the iron metal, from the nail, which goes into solution in the process is oxidized, so that the quantity of ferrous chloride finally present comes not only from the reduction of ferric chloride to ferrous chloride, but partly also from the oxidation of iron to ferrous chloride. Ferrous chloride can finally be oxidized back to ferric chloride by passing chlorine gas into the solution. Thus in these oxidations and reductions we have nothing whatever to do with the element oxygen, but have learned that chlorine is an effective oxidizing agent, and that reduction may involve the removal of other elements than oxygen.

(Note.—For a more complete account of this subject the reader is referred to any of the standard works on chemistry. It will be, in fact, an excellent idea if he will extend his reading in these chemistries to cover such subjects as valency, the ionic theory, and molecular and atomic weights, which are not within the scope of the present work.)

CHAPTER III

LIGHT AND CHEMICAL REACTION

WE have learned that some chemical reactions require, in order to start, nothing more than the mere contact of the substances involved, at the ordinary temperatures. On the other hand, of those reactions which need to be initiated by the application of energy to the reacting factors, there are two kinds: first, such reactions as, when once started, develop greater or less quantities of heat energy by means of which they are enabled to proceed to a finish, one or other, or sometimes both, of the factors being used up; and, second, those which continue only so long as sufficient energy is applied, the energy being absorbed in the process. The terms energy, and heat energy, are here employed in the most general sense to include all those vibrations of the ether, whereby radiant energy is transmitted through space, and without reference to the wave-length of the vibrations. In the present chapter we shall limit ourselves to a consideration of the energy of the shorter wave-lengths, and illustrate and discuss some typical chemical reactions which are originated by the energy of light, since it is these photo-chemical reactions, as they are called, which are of primary consequence in the making of pictures by photographic methods.

That reactions of this kind are continually going on in nature will readily be seen if we merely mention the tanning of the skin by exposure to sunshine, the fading of colors in bright light, and the process referred to in the preceding chapter by which chlorophyll of the plant world, absorbing the energy of light and utilizing it, decomposes the carbon dioxide of the air. Perhaps we may get some idea of the amount of work involved in this operation, if we stop to consider how great a quantity of heat is given out when wood is burned, remembering that the heat energy set free in the burning of each pound of carbon to form carbon dioxide is exactly equivalent to the energy absorbed in the separation of this amount of carbon. But the substances concerned in these photo-chemical reactions are too complex and the changes too complicated for our present consideration. It will be well, therefore, for us to begin with something simpler and more easily comprehended.

Certain of the elements are affected in a very peculiar way by light. For example, the common form of sulphur, roll sulphur, or brimstone, occurs in rhombic crystals and is very soluble in carbon disulphide. But upon exposure to light it is changed to an amorphous condition (non-crystalline) in which it is no longer soluble in the solvent mentioned, and at the same time heat is given out:

Sulphur (rhombic) + Light (Violet)
= Sulphur (amorphous) + Heat (Infra-red)

The element phosphorus goes through a similar change in which the two varieties are even more differentiated from each other. Phosphorus may be purchased either in waxy, yellowish-white sticks or as a red powder. Yellow phosphorus melts at 44.4 degrees centigrade, is soluble in carbon disulphide, and is extremely poisonous. Matches were formerly manufactured with this yellow form, and workmen in match factories were subject to a peculiarly dreadful disease. When the yellow form is exposed to light, particularly the blue, violet, and ultra-violet rays, it is thereby converted to the red modification, with the liberation of heat. Red phosphorus does not melt even at red heat, is insoluble in carbon disulphide, and is not poisonous. After much vigorous objection by the match manufacturers because of the greater cost of red over yellow phosphorus, laws were passed several years ago prohibiting the use of the poisonous yellow form, and matches are now made out of the harmless red variety:

Phosphorus (yellow) + Light = Phosphorus (red) + Heat

Selenium is another element which is light sensitive. It can be prepared as a bright red, amorphous powder which is soluble in carbon disulphide, melts at 125 degrees centigrade, and is a non-conductor of electricity. By the action of violet light, red selenium is changed to a dark gray, crystalline, metallic form. This is insoluble in carbon disulphide, melts at 217 degrees centigrade, and is a variable conductor of the electric current according to the intensity of light thrown upon it:

Selenium (amorphous) + Light
= Selenium (metallic) + Heat

Several interesting uses have been made of the peculiar property of the metallic selenium, namely, its variability in conductivity produced by changes in the illumination. The resistance of a "selenium cell" may be as much as two hundred times as great in the dark as in the light. By use of such cells in electrical circuits, motors can be started and stopped by a beam of light, or signal lights caused to operate automatically, the gas or current being turned on by the coming of darkness and turned off again with the daylight. Perhaps the most wonderful application of this light reaction is in the transmission of photographs by telegraph.

The three photo-chemical reactions just described are evidently quite different in their nature from such a reaction, for example, as the reduction of ferric to ferrous chloride, which we shall presently consider. In some so far unexplained way they appear to be readjustments in the energy conditions prevailing in the molecules of these light-sensitive elements.

If precisely equal volumes, measured under identical conditions of temperature and pressure, of the two gaseous elements hydrogen and chlorine are put into a glass jar and kept in total darkness, the amount of hydrogen chloride formed in a given time by the chemical union of these elements will be inappreciable. Practically we may say that in the absence of light no reaction occurs. When, however, the jar is brought out and set in a very weak light, the hydrogen and chlorine begin slowly to combine, and after the lapse of sufficient time there will be found in the jar only hydrogen chloride gas. If the jar be put in a more brightly illuminated place, the reaction becomes more rapid. By exposing it to direct sunlight, indeed, it becomes so much accelerated as to be violently explosive, and the glass jar, unless very stout, will probably be shattered. In performing this experiment it is usual to mix the gases in the dark, wrap the jar completely in a black cloth to which has been attached a long string, and set the apparatus in the sunlight. The experimenter thereupon retreats to the other end of the cord and jerks away the protecting cloth. The explosion follows instantly, and is occasioned by the fact that when hydrogen and chlorine unite a tremendous evolution of heat takes place. Since the product, hydrogen chloride, is also gaseous, it expands with great pressure under the influence of the liberated heat. It is needless to say, perhaps, that this experiment is a very dangerous one. The reaction is:

Hydrogen + Chlorine + Light = Hydrogen chloride + Heat

Hydrogen iodide is a gas similar in many respects to the hydrogen chloride we have just been discussing. Its solution in water is colorless, and is commonly called hydriodic acid. When such a colorless solution is exposed to both the oxygen of the air and light, it turns brown. Light causes decomposition of the hydrogen iodide, setting free iodine, which in solution has a brown color, if water is the solvent. The hydrogen combines with oxygen from the air, forming water, so the reaction may be expressed:

Hydrogen iodide + Oxygen + Light = Iodine + Water

Blue light is most effective in bringing this reaction about. But we must note in this case that without the presence of oxygen the reaction could not go on, as hydrogen and iodine would recombine directly they were separated, being both chemically active substances. It would probably be more correct to say that under such circumstances both these actions would be going on simultaneously, hydrogen and iodine recombining to form hydrogen iodide as fast as the latter was being decomposed. That is, we might write the reaction in the following way:

Hydrogen iodide $\rightleftharpoons$ Hydrogen + Iodine

The direction of the arrows signifies that both reactions are proceeding at the same time. Such a reaction is said to be "reversible." But when oxygen is at hand, the hydrogen unites with it in preference to iodine, and thus the decomposition of hydrogen iodide is enabled to go on, reaction progressing only from left to right in the above equation. As we shall see, there are other photochemical reactions in which the presence of some additional substance is required in order that light may produce the effect. Photographically speaking, we should say that this extra substance is a "sensitizer," the decomposable material, such, for example, as hydrogen iodide, being "insensitive" in the absence of the "sensitizer."

Another reaction of decomposition brought about by light occurs with ferric oxalate, a compound which is of considerable photographic importance. When discussing the subject of oxidation and reduction, we showed how by suitable means a ferric salt is reduced to ferrous salt, and the ferrous oxidized back to ferric. Light is able to perform this reduction with ferric oxalate, ferrous oxalate being produced, and carbon dioxide escaping.

Experiment 5. Expose to strong sunlight for half or three quarters of an hour a few of the brownish scales of ferric oxalate, and at the expiration of this time look for any change which has been produced. Save the material for Experiment 7. It will be well for us here to learn how to detect the presence of ferrous and ferric iron in substances, since in the use of ferric oxalate for photographic purposes it is very necessary to have no ferrous salt present. If the ferric oxalate is from old stock or has been handled much in the light, it is very likely to have suffered reduction in part, and this will render it useless. The brown color of the bottle in which it is bought and must be kept is intended to protect it from the action of all light except that transmitted by the brown glass. We will first make an experiment to show how ferric salt is detected.

Experiment 6. Dissolve in 5 cubic centimeters of water a small crystal of ferrous sulphate, add a few drops of dilute sulphuric acid and shake up this solution in the test tube for several minutes. Since there is air in the test tube above the solution and ferrous salt is very readily oxidized by air, this shaking will give some of the ferrous sulphate in the solution an opportunity to be oxidized to ferric sulphate. We might do the same thing more quickly by adding to the liquid a drop or two of nitric acid, which is a good oxidizer. In either case we shall have the same result in effect, as it may be represented:

Ferrous sulphate + Sulphuric acid + Oxygen
= Ferric sulphate + Water

In the presence of nitric acid there would be formed also some ferric nitrate.

Next take a very small crystal of potassium ferrocyanide, or as the druggist would probably call it, yellow prussiate of potash, break it into still smaller bits and dissolve a minute piece in 5 cubic centimeters of water. This will be a very dilute solution. In the same way make 5 cubic centimeters of a dilute solution of potassium ferricyanide, or red prussiate of potash. Take about a cubic centimeter of the prepared solution containing ferric sulphate in a clean test tube, dilute it with water to about 5 cubic centimeters, and add a few drops of the dilute potassium ferrocyanide. The fine blue color, which is Prussian blue, is due to the formation of ferric ferrocyanide, and is always obtained when solutions of potassium ferrocyanide and a ferric salt are mixed. Thus the blue coloration is a chemical test for ferric iron. Now boil 5 or 6 cubic centimeters of water in a clean test tube, to expel all oxygen which is in solution in the water, cool without shaking (to prevent as much as possible the water from absorbing more oxygen), and dissolve in it a very small, clear crystal of ferrous sulphate. As quickly as may be, add to it a few drops of potassium ferricyanide solution. The blue color which appears in this case is Turnbull's blue, and is always obtained when solutions of potassium ferricyanide and a ferrous salt are mixed, and is therefore a chemical test for ferrous iron.

So, to repeat, ferrocyanide gives blue with ferric iron salts; and ferricyanide gives blue with ferrous compounds. By writing out these reactions in equations we shall see that they are reactions of metathesis, as follows:

(1) Ferric sulphate + Potassium ferrocyanide
= Ferric ferrocyanide + Potassium sulphate
(2) Ferrous sulphate + Potassium ferricyanide
= Ferrous ferricyanide + Potassium sulphate

If the experiments have been carefully done according to directions, it will be apparent that these tests are very delicate.

Experiment 7. Treat in a test tube with 5 or 6 cubic centimeters of water a little of the ferric oxalate which was exposed to light in Experiment 5. If any powder remains undissolved, add a crystal or two of potassium oxalate to get it into solution. Shake the tube, and to its contents add a few drops of potassium ferricyanide solution prepared in Experiment 6. Blue coloration indicates the presence of ferrous iron. Compare with this the action of ferricyanide upon a fresh, cold solution of ferric oxalate. If the latter compound is pure, there will be no blue color developed in salt which has not been exposed to light.

The question whether ferric oxalate contains any ferrous salt as an impurity must be answered upon the basis of what takes place immediately when the mixture of the two solutions is made and not upon what may happen after this mixture has stood for some time:

Ferric oxalate + Light = Ferrous oxalate + Carbon dioxide

If the ferrous oxalate is put away in the dark in contact with the air, ferric oxalate forms again by oxidation.

Experiment 8. Dissolve a crystal of uranium nitrate in 5 cubic centimeters of water, spread about half of this solution upon a piece of paper, using a sized paper such as writing paper, and lay it aside in a dark place to dry. To the remainder of the uranium nitrate solution add a few drops of dilute potassium ferrocyanide, and note the blood-red color produced. As soon as the prepared paper is dry, expose it to strong sunlight for a few minutes and then flow over it a little of the potassium ferrocyanide and compare the result with the preceding.

Uranium salts are extremely sensitive to light, uranyl compounds being reduced to uranous. Potassium ferrocyanide forms with uranyl nitrate red uranyl ferrocyanide. When exposed to light, uranyl salts are reduced, and then with ferrocyanide the green uranous ferrocyanide is obtained.

Experiment 9. Make up a little potassium dichromate solution, coat with it a piece of sized paper, and dry it in the dark. When dry expose it to sunlight in a printing frame under a negative for five minutes. On examination it will be seen that opposite the thin places in the negative the orange color of the dichromate has turned brown, but beneath the dense parts there is little or no color change.

In order to investigate this reaction a little further and to find out if possible what may have happened to the chromium compound, let us take 4 or 5 cubic centimeters of ferrous sulphate solution, add to it a little of our solution of potassium dichromate and then make the test with potassium ferrocyanide for ferric iron. We shall discover by this means that potassium dichromate is a good oxidizer, since it quickly changes ferrous sulphate to the ferric salt. Since the dichromate oxidizes ferrous iron, it must itself be reduced. Now, returning to the paper coated with dichromate, we have here an oxidizing agent in contact with the materials of which the paper and sizing consist. These are organic substances, principally cellulose in the paper and possibly starch in the sizing. Both these substances are comparatively easily oxidized, and consequently it becomes plain that in the coated paper we have dichromate, a good oxidizer, in contact with excellent reducing agents. So when light energy was brought to bear upon this state of things, the organic matter was oxidized and the dichromate reduced. Without the organic substances there would have been no reduction of dichromate, and so the paper and sizing act as sensitizers. There is reason to think that the chemical reaction which takes place under the influence of light may be expressed thus:

Organic matter + Potassium dichromate + Light
= Chromic oxide + Potassium hydroxide
+ Organic matter (partly oxidized)

Another reaction with dichromate has interesting applications in printing processes to be discussed later.

Experiment 10. Make up a solution of about 0.5 gram of potassium dichromate in 5 cubic centimeters of water. Soak in a very little cold water 0.5 gram of gelatine; when it has swelled, add more water so that the gelatine may dissolve by gentle heating. Take about 5 cubic centimeters of the gelatine solution, add to it a cubic centimeter of dichromate solution, mix thoroughly, and coat some of the mixture on a piece of sized paper. Expose the dried paper for two or three minutes under a contrasty negative, and observe the effect. Wash the paper in warm water and observe that all the gelatine cannot be washed off the paper.

Gelatine is an organic substance, akin to the proteins which are essential constituents of food-stuffs. It is made from the bones and cartilages of animals. It is soluble in cold water, ordinarily, and its solubility is much increased by gentle heat; but by long continued boiling it tends to become more insoluble. A solution of gelatine differs in a marked way from one of such a substance as sodium chloride or silver nitrate. When solutions of these salts are allowed to stand, the solid material is, by the gradual evaporation of the water, caused to deposit in the form of crystals. Also if a partition of parchment is placed in a dish so that a salt solution can be poured in one side and pure water in the other, the parchment serving to keep the two liquids separate, after a little while it will be found that the salt has passed through the parchment into the water. This process is known as diffusion, and all substances that form crystals have the power of diffusing through such a membrane. Crystallizing substances are often called crystalloids. But if these experiments are repeated, using a solution of gelatine instead of salt, in the first place no crystals will be secured under any circumstances, but rather the gelatine solution will "set," or, as the housewife calls it, "jelly." In the second place, none of the gelatine will be able to pass through the membrane; it cannot diffuse as a salt is able to do. As distinguished from the crystalloids, gelatine belongs to the class of substances called "colloids." Gum arabic is another example of a colloid, and one that also has photographic uses.

Referring now to the experiment just performed, we learned that light possesses the power so to affect a mixture of gelatine and potassium dichromate that the gelatine, previously quite readily soluble in water, becomes insoluble. One circumstance in the way this reaction was conducted is worthy of special mention. Since the gelatine-dichromate mixture was spread as a coating upon the surface of paper, it is evident that wherever the light was transmitted by the negative it, so to speak, fell first upon the outer surface of the coating. Then, as it passed into the gelatine film, it was more and more absorbed. Consequently its energy was gradually diminished in proportion to the depth to which it penetrated. Therefore the maximum effect of this light reaction occurs at the outside surface of the film, the greatest degree of insolubility being produced there; and the insolubility diminishes as the surface of the paper is approached. So we may have as the result of the exposure of such a film to light an outside layer of insolubilized gelatine protecting, as it were, layers of much greater solubility which lie beneath it. We may as well note, also, that the more soluble layers are protected upon the other side by the paper. The bearing of these observations we shall have occasion to take up in a later chapter.

The photo-chemical reaction which historically was the first to be discovered, we have reserved for the conclusion of our theoretical discussion. It was in the sixteenth century that the alchemists noted the change produced in silver chloride by the action of light, although they were unable to form any adequate idea of the nature of this change. Not until the last quarter of the eighteenth century, by the Swedish chemist Scheele, was it shown that silver chloride when exposed to light under water loses chlorine. In his experiments Scheele found that after light had produced its effect upon the compound, the water contained chlorine in solution, which would form with silver nitrate a precipitate of silver chloride again. By treating with ammonium hydroxide the residue of darkened silver chloride, Scheele also got what he supposed to be metallic silver. So he concluded that light had reduced the silver chloride to elementary silver, gaseous chlorine escaping in the process. Perhaps it will be of interest to repeat this experiment of Scheele's made in the year 1777.

Experiment 11. Prepare a two per cent. solution of silver nitrate by dissolving 0.2 gram of the solid in 10 cubic centimeters of water. Warm, and then completely precipitate the silver from this solution as silver chloride by adding hydrochloric acid until no further change is observed. There should now be present a slight excess of hydrochloric acid. Wash the precipitate thoroughly by decantation, keeping it away from strong light as much as possible. Prove, by testing as in Experiment 3, that all soluble chloride has been washed from the precipitate. If kept away from the light, the silver chloride will still be white. Treat a small portion of it in another test tube with a little dilute ammonium hydroxide, and observe that the solid is wholly dissolved. Silver chloride is very soluble in ammonium hydroxide. Cover the remainder of the precipitate with 3 or 4 cubic centimeters of chloride-free water and expose for some little time to strong sunlight. After the exposure, pour off the water into another clean test tube. Add a drop of silver nitrate solution to this water, and look for the formation of white silver chloride. If any is formed, the chlorine must, if the work has been carefully done, have been separated by the light from the original silver chloride. Cover again with a little water the darkened residue and treat it with ammonium hydroxide until there is no further solvent action. The dark powder which is left is what Scheele took for elementary silver. It is not the element, however, for it is known to contain chlorine. It is now generally considered to be either a sub-chloride of silver or a solid solution of silver in silver chloride. Whichever may be the fact, it will for our purposes be enough to call it silver sub-chloride, since practically it is silver chloride which has been robbed by the light of some of its chlorine. Thus, when light is allowed to act upon silver chloride, the compound is, as it were, given such a shaking as to set free part of its chlorine. The shorter wave-lengths are the most effective, and particularly those in the region of the spectrum known as the ultra-violet. Photographically speaking, these are the actinic rays. The reaction may be expressed:

Silver chloride + Light = Silver sub-chloride + Chlorine

Experiment 12. Prepare silver bromide in an exactly similar manner as the chloride was made in Experiment 11, using potassium bromide as the precipitant. Try the solvent action of ammonium hydroxide upon a small portion of the precipitate and note that silver bromide dissolves, but not so readily as did the chloride. Expose some of the salt to light and observe the darkening. Reaction:

Silver bromide + Light
= Silver sub-bromide + Bromine

Experiment 13. Make another experiment similar to the preceding, except that silver iodide is precipitated, washed, and examined, using potassium iodide instead of the bromide. Compare the solubility of silver iodide in ammonium hydroxide with that of silver bromide and silver chloride in the same reagent. Silver iodide is practically insoluble in the ammonia. Observe that upon very carefully washed silver iodide light produces little effect. Add a drop of silver nitrate solution and note that darkening proceeds rapidly.

Silver nitrate is therefore a sensitizer for the iodide. That it acts in the same capacity with the chloride and bromide may be quickly determined by experiment. The explanation of this action on the part of silver nitrate is as follows: All three of these photo-chemical reactions are essentially reversible, *i.e.*, for example, silver sub-bromide and liberated bromine tend to recombine as fast as they are formed. In the cases of chloride and bromide, light energy is powerful enough to cause decomposition unaided, although it proceeds with much greater rapidity in the presence of silver nitrate or any other substance which will take up chlorine or bromine. With the iodide, on the other hand, there must be present some "sensitizer" in order that the reaction may go on. Reaction:

Silver iodide (with sensitizer) + Light
= Silver sub-iodide + Iodine

In the types of chemical reactions described in Chapter II, together with the photo-chemical experiments performed and discussed in the foregoing chapter, we have the basis of all the operations of the photographic art. It is to the application of the principles here so briefly set forth that we now turn in the succeeding chapters.

CHAPTER IV

APPLIED PHOTO-CHEMISTRY OF SILVER SALTS

A COMPARISON of the action of light upon the three silver salts, the chloride, bromide, and iodide, shows that the visible effect is greatest with chloride and least with iodide. But since, as we know, it is not metallic silver which is the product of this reaction, but only the relatively unstable sub-compounds, there must be provided some means whereby the partial reduction initiated in this photo-chemical process may be carried to a finish in completely reduced silver. A little experiment upon the interaction of reducing agents and silver salts will serve to throw considerable light upon this phase of the problem.

Experiment 14. To a few cubic centimeters of silver nitrate solution, add a little ferrous sulphate in solution and observe the immediate separation of silver as a black powder. Ferrous sulphate is a powerful reducing agent. Next acidify a little ferrous sulphate solution by adding a drop or two of dilute sulphuric acid, and treat with this another portion of silver nitrate solution. The reduction of silver takes place very much more slowly when acid is present. Next prepare small quantities of thoroughly washed silver chloride, silver bromide, and silver iodide, taking care to keep them away from the light as much as possible. Treat a portion of each salt with acidified ferrous sulphate. There is little reduction when the silver salt has not been subjected to the action of light. Spread out upon glass plates more of the three salts and expose them for five or ten minutes to strong sunlight. Then put a few drops of the acidified ferrous sulphate upon each salt and note that reduction at once takes place. Finally expose to light for a very brief interval, not over half a minute, the rest of the silver salts and treat with acidified ferrous sulphate. In this case it is to be noted that, whereas the chloride is the most visibly affected by light and the iodide is the least affected, reduction by ferrous sulphate of the exposed substances is most marked with the iodide. Reactions:

(1) Silver nitrate + Ferrous sulphate
= Silver + Ferric sulphate + Ferric nitrate
(2) Silver bromide + Light
= Silver sub-bromide + Bromine
(3) Silver sub-bromide + Ferrous sulphate
= Silver + Ferric sulphate + Ferric bromide

From the experiment it might naturally be inferred that silver iodide would be the most sensitive medium with which to make a coating. In practice a mixture of bromide and iodide gives the best results, a very much greater proportion of bromide than of iodide being used. In the past, various different methods have been employed for supporting the light-sensitive film, and for fastening it to its support. Since we are not here concerned with any of these older methods, largely obsolete at the present time, the reader is referred for detailed accounts of them to those works on photography in which is given a historical survey of the subject. The progress of the art has consistently been in the direction of increased sensitiveness. Inasmuch as the general principles underlying all the different procedures have been the same, we shall not only save time but arrive at a satisfactory understanding of the matter by confining ourselves to the discussion of present-day practice.

As supports for the sensitive body there are now in use principally three different materials, glass plates, celluloid sheets, either cut in rectangles or in rolls, and a considerable variety of papers. These may be divided into two groups, the glass and celluloid on the one hand and the papers on the other. The former are employed in the first part of the photographic process, namely, the making of the negative; the latter chiefly in the second part, the making of the print. This distinction may reasonably be made for our convenience, but cannot be considered a hard and fast rule, for paper negatives are often made, and the use of glass and celluloid for lantern-slides and transparencies and of celluloid for motion-picture reels must be taken into account. But by this classification we are enabled to treat separately the principles involved in the making of negatives, leaving the numerous printing processes for later chapters. Of the relative advantages of glass plates and celluloid sheets as supporting media, it is needless here to say more than a word. Glass is heavy and celluloid is light when it comes to carrying large quantities, and the question is easily answered by the factor of weight, taking into account also the convenience of the roll form in which celluloid film is supplied. For the amateur who gets beyond the "snapshot" stage and begins really to be initiated into the photographic "mysteries," glass plates are almost certain to be found most desirable, partly on account of their lower price, but chiefly because they can be had of different qualities to suit different purposes.

So far, we have considered the light-sensitive substance and the foundation upon which it is laid down. Now it remains to bring these two factors together.

Whatever be the nature of this foundation, the link that binds them together is of the same general character. Confining ourselves to glass as a basis for simplicity's sake, we find that the ordinary "dry plate," or glass plate, consists of a coating of gelatine containing the silver salt and sometimes other materials, spread upon one surface of a rectangle of clear, uniform glass. The next experiment illustrates the nature of this gelatine coating.

Experiment 15. Soak in 25 cubic centimeters of cold water contained in a small conical flask 1.5 gram of gelatine. As soon as the gelatine has swelled, dissolve it by gentle warming. Next dissolve 3.5 grams of silver nitrate in 5 cubic centimeters of water and mix thoroughly with the former solution. In 10 cubic centimeters of water dissolve together 0.1 gram of potassium iodide and 3.0 grams of potassium bromide. Warm the gelatine mixture and, by the red light of the darkroom, add to it the solution of bromide and iodide drop by drop, shaking it up thoroughly after each addition. By this means there are formed everywhere throughout the mass of gelatine minute solid particles consisting of silver bromide and silver iodide. Such a mixture of liquid with finely divided solid particles suspended in it is called an emulsion. Set the little flask in a dish containing boiling hot water and keep it at that temperature for half an hour, protecting it from all white light during this operation. Transfer the emulsion to a small wide-mouthed bottle such as a vaseline jar, for example; stand the jar in cold water, and allow the emulsion to set to a firm consistency. It will now be in order to consider just what the emulsion contains. According to the proportions given for silver nitrate and potassium bromide and iodide, there is an excess of the potassium salts present above the amount required to form silver bromide and silver iodide with the given quantity of silver nitrate. Consequently there are now present in the gelatine emulsion the unused potassium salt and the potassium nitrate formed in the metathesis. It is necessary to free the emulsion from these soluble salts. As it is very sensitive to light, all these operations must be performed in the darkroom. When the emulsion has set thoroughly, take it from the jar and put it into the middle of a small square of white mosquito netting. Gather up the corners, twist them together, and squeeze the jelly through the cloth into a dish of cold water, holding the cloth under the surface, which will prevent the shredded emulsion from running together again. Put the shreds back in the cloth, pour cold water liberally over them, and let them soak in cold water for a quarter of an hour. Repeat the process of squeezing through the cloth and washing, after which allow the water to drain off, and then by gentle heat melt up the emulsion and pour a portion of it upon a small, clean, dust-free glass plate, tilting the plate in such a way as to allow the emulsion to run completely over its surface. Any excess of gelatine may be run from one corner back into the jar. Put the plate down level to permit the emulsion to set and dry. When thoroughly dried this "dry plate" can be exposed under a negative, developed, fixed, and washed in the usual way. Coat several more small squares of glass with the rest of the emulsion which has been prepared; when dry they may be stored in a light-proof box for further experiments.

All the reactions which take place in the operations of making and exposing this plate have already been described. The reason for using an excess of bromide and iodide in the manufacture of photographic emulsions is that silver nitrate and gelatine interact chemically. The compound formed by their reaction will also react with the bromide and iodide salts to form silver bromide and silver iodide. But, were there an excess of silver nitrate used, this excess could not be washed out, since the silver would be chemically combined with the gelatine. On the other hand, when the excess of bromide and iodide is added, all the silver present in the gelatine solution reacts by metathesis with them. Then the excess of soluble potassium salts can readily be removed by washing. If the solutions out of which the emulsion is made are comparatively cold when mixed together, suitable examination will show that the particles of insoluble silver salt are very minute. A plate coated with such an emulsion will be relatively "slow," *i.e.*, it will require a long exposure to light to get a satisfactory image. In the manufacture of dry plates it was early discovered, first, that they could be made more rapid by allowing the emulsion to stand at a temperature of about 30 degrees Centigrade for some days, a process called ripening; and second, that a similar ripening could be secured by keeping the emulsion at the boiling temperature for only a few minutes; and finally, that simply the addition of ammonium hydroxide produced the same result without any heating at all. The reason for the physical difference between the unripened and the ripened emulsion can very easily be shown by a simple experiment.

Experiment 16. Treat a little cold dilute solution of silver nitrate with a few drops of dilute hydrochloric acid without shaking. The precipitated silver chloride is seen to be in a very finely divided state. Now add more of the acid until precipitation is complete and warm the mixture to boiling. Shake it vigorously.

The precipitate now is gathered in larger bunches, or, as the chemist says, is flocculent. So silver chloride may be formed in a very fine state of division, but the minute particles, when heated and shaken tend to collect together into larger aggregations. The same thing is true of silver bromide and silver iodide. In general, the more rapid the emulsion the larger the particles of silver salt in it, or, as the photographer says, the coarser the grain of the plate. Thus the slower plates have the advantage over fast emulsions of fineness of grain, which is a point that it is sometimes useful to remember. It is not now considered that the rapidity of an emulsion is dependent upon the size of its particles, but that the increase in size is an accessory circumstance to the ripening.

We may now review briefly the reactions which take place when one of our home-made dry plates is submitted to the action of light for a short interval of time. Examination after the exposure discloses no perceptible change in its appearance, but from our previous experiments we may be sure that, wherever the light has fallen upon the sensitive emulsion, silver bromide has been altered to silver sub-bromide and silver iodide, to sub-iodide. In the case of the iodide we have learned that the condition necessary for this action is that there should be present some substance which is capable of reaction with the liberated iodine. And with the bromide also the action is very much facilitated by the presence of a bromine-absorbent, in order to prevent the reverse reaction from occurring. Gelatine, as it fortunately happens, is such an absorbing substance. Thus when the light energy is received in the emulsion, it is transformed into the chemical energy of separation of bromine and iodine from bromide and iodide respectively, and the free bromine and iodine immediately interact with the gelatine. In this way they are safely removed from the sphere of chemical action. It is chiefly due to this fact that the present day photographic emulsion is so extremely rapid. That this partial reduction has been effected by the exposure to light may finally be demonstrated by flowing over the plate, in the darkroom, a little ferrous sulphate solution acidified with sulphuric acid. Any portions of the plate which were in the exposure protected from the light will be unchanged, but wherever the light reached the emulsion an immediate reduction of the sub-salt to metallic silver will occur.

If in the exposure the whole surface of the plate is not uniformly illuminated, but different portions are subjected to light of different intensities, in the various regions different amounts of sub-salt are formed. This follows from the fact that the quantity of silver salt reduced to sub-salt is directly proportional to the amount of light absorption. But since the whole of the plate was exposed for the same length of time, the quantity of light absorption is directly proportional to the intensity. So, when the plate is developed by ferrous sulphate, in those portions affected by more intense illumination there is a proportionately greater amount of silver reduced than in the parts affected by less illumination. At the upper limit, or maximum effect, all the silver in the part of the emulsion concerned will be reduced to metallic silver. In the minimum, no reduction whatever will take place. And between these two limits there is possible theoretically an infinite number of steps. We have here an explanation of the exquisite gradation of tones which forms one of the pre-eminent characteristics of the photographic print. Practically the number of grades is limited on account of the fact that the particles of silver salt have appreciable size, and therefore the number of particles in a given area varies with the size of the individual particles. Thus the depth of a given tone depends upon the number of particles of silver salt reduced to silver, and the least possible difference in tone is that due to a difference of one in the number of particles. Therefore a coarse-grained emulsion, or other things being equal, a rapid one, necessarily gives less gradation than a fine-grained, or slow, emulsion. ✓

So far we have considered only the effect of white light. But, as we know, white light consists of a mixture of an infinite number of different wave-lengths in the luminiferous ether, and we have previously stated that some photo-chemical reactions are especially promoted by particular sets of wave-lengths, such as, for example, the change of yellow phosphorus to its red modification, in which the blue, violet, and ultra-violet rays are effective. If we should expose some of our home-made dry plates to the different sets of wave-lengths, or colored rays, of the spectrum, which is produced by passing a beam of white light through a prism, a very long exposure indeed would be necessary to produce upon development a perceptible effect with the infra-red rays, which are invisible of course because their wave-lengths are too great. With the red rays hardly less exposure would be needed to give an appreciable image. The yellow would require somewhat less. But even in the green the exposure would yet have to be markedly long, although very much shorter than with the red rays. When we came to the blue and violet, however, we should find the sensitiveness of the plate as notable as was its lack of sensitiveness at the other end of the spectrum. And in the ultra-violet, invisible because of the shortness of wave-length, the sensitiveness is but a little diminished. To put the matter in another way, if a strip of dry plate is exposed to the whole spectrum at once, little or no effect is produced by the infra-red and red rays, and very little by the orange and yellow even with a long exposure. A more pronounced effect begins in the green, the maximum occurs in the blue-violet, and there is a falling off in the ultra-violet. The sensitiveness of the eye to the various portions of the spectrum is quite different from this. The infra-red, it is true, makes no impression upon the sense of sight, but beginning with the red its sensitiveness rapidly increases to a maximum in the yellow. From here the brightness diminishes again until it reaches zero once more in the ultra-violet. To the eye the brightest part of the spectrum is the region from orange through yellow to green, parts that are practically dark to ordinary photographic emulsion; whereas to the emulsion the brightest portion lies in the blue-violet, which is comparatively dark to the eye, and the brightness extends beyond into the ultra-violet, which is totally black to the eye. Since daylight ordinarily contains a preponderance of blue, violet, and ultra-violet rays, and red, orange, and yellow rays act to no appreciable extent upon the ordinary emulsion, a plate coated with it and exposed in the camera to a landscape, for example, registers the view as it would appear to an eye whose sensitiveness instead of having its maximum in the yellow has this maximum in the blue-violet, the same as the plate. The landscape, too, commonly has an abundance of green foliage, to the rays from which the emulsion is but little sensitive. Using such emulsion, it is a matter of no small difficulty photographically to make a landscape which will show the verdure in foreground, the distance, and the sky as these factors appear to a discriminating eye. To represent the blue sky and even the billowy clouds by a practically uniform expanse of white paper, and the varied greens of grass and trees by dense blackness is to give a very untruthful rendering.

The position of the maximum sensitiveness of the photographic emulsion cannot be moved from the blue-violet region, but by incorporating with it certain dyes, it is possible to produce secondary maxima in other regions of the spectrum. Thus, by treating one of our home-made plates with a solution of the blue dye cyanin, and allowing it to dry again, we shall have a plate which is sensitive far into the red. A purple solution of pinacyanol also gives red-sensitiveness and great rapidity to the plate, but one so prepared must be handled and developed by a green light, for it is quite insensitive to the green rays. With pinaverdol there is a great increase in the sensitiveness to the orange, yellow, and green. If these dyes are added in the process of manufacturing the emulsion, the plates so prepared have fair keeping qualities. Plates thus made keep better, but are not quite so color-sensitive as those which are dyed just before using. The action of these dyes in producing red, yellow, and green sensitiveness is not wholly clear. Possibly they form very complex silver compounds which are specially sensitive to the respective rays. Inasmuch as it is the light absorbed which performs the chemical work, the suggestion has been made also that perhaps the dye, after absorbing its particular rays, is able to give out again the energy so stored up. Where these rays act upon the plate, therefore, an increased reduction of silver salt occurs. Color-sensitized plates are sold under the names isochromatic, orthochromatic, panchromatic, etc. But as already stated, the maximum sensitiveness to the violet end of the spectrum cannot be changed by any means that has so far been discovered, and even when red-sensitiveness has been increased as much as possible, the blue-sensitiveness still overbalances it. For this reason it is necessary in order to secure the full benefit of color correction to cut out most of the blue, violet, and ultra-violet rays from the light which is transmitted to the plate. This is done by putting over the lens a piece of yellow glass, called a ray filter or ray screen. Being, as we say, colored yellow, this glass has the property of absorbing the rays from the blue end of the spectrum and so protects the plate from their action. A disadvantage in the use of ray filters lies in the fact that the artificial sensitiveness of the plate to the red cannot be made as great as its natural sensitiveness to the blue. With the ray filter the plate is therefore much less rapid than without it.

Thus far, in speaking of the exposure of our emulsion to light, we have been concerned merely with that duration of exposure which would give an appreciable image by use of such a reducing agent as ferrous sulphate, for example, or as we should say, photographically, upon development. If we now inquire what will be the effect of submitting a plate to exposures of various durations, we shall obtain some very interesting results. Let us suppose that with the conditions of illumination, the size of stop it is desired to use in the lens, and the sensitiveness of the plate employed, an exposure of one second would give us what the photographer is wont to call a "perfectly timed" negative. We recognize at once that, if we allow but a very small fraction of a second for the exposure, there will not be time enough, or much better, not energy enough in the light which reaches the plate, to affect more than a very small proportion of the sensitive silver salt. Thus, we would get an "under-exposure," a sort of negative generally characterized by a few dense patches corresponding to the highest lights in the object, and clear glass, giving none of the details corresponding to the deepest shadows. By making a series of exposures, each one, say, double the preceding, we find as we progress towards the standard exposure of one second that finally a point is reached where a negative can be developed which compares quite favorably with one perfectly timed, and yet the duration of the exposure which produced it was considerably less than the normal. Furthermore, by carrying our series of exposures up above one second, we can discover an upper limit at which a passable negative will also be secured. This range of exposures within which acceptable negatives can be made is commonly called the "latitude" of the emulsion, and varies somewhat with different brands of plates and with different speeds of emulsion. It is the safeguard of the amateur. In general, slower plates have greater latitude than the faster ones. But above this upper limit, the negatives which result become more and more disappointing. They are indeed "flat, stale, and unprofitable." The best cure for overexposure, as it is also for underexposure, is to throw away the plates and try again, using an exposure-meter to determine the correct time.

But suppose we allow light to act for periods successively very much greater than the normal one second. Presently upon development one of them will come up a positive, instead of a negative, highlights in the plate now corresponding to highlights in the object, and shadows to shadows. This being the reverse of what usually happens, is known as the "reversal" of the image. A further increase in the length of exposure will give a negative again; still more time, a positive; and yet more, a negative.

Experiment 17. Under such conditions as would normally demand an exposure of about one second, submit an ordinary plate or film in a camera to the action of light from some object for about one minute, and develop as usual. Give to another plate an approximately normal exposure; in the darkroom place it for two minutes in a dilute solution of potassium dichromate, rinse off the dichromate, and then try to develop it into a negative. Consider that the silver salt which has been partially reduced by light has first been subjected to the action of a good oxidizer (dichromate) before the application of the developer. Give to a third plate an exposure approximately normal. This will naturally develop into a negative. When it has been developed, rinse, and put it into a dilute solution of dichromate, and carry it out, in the tray, into daylight. As soon as the plate has bleached out, wash it in running water for half a minute and develop it again, in daylight, with the same developer as before used. The image should be reversed.

Any other soluble oxidizing agent, such as potassium permanganate, hydrogen dioxide, etc., would do just as well as the dichromate. In explaining this curious behavior of the light-sensitive emulsion, we must take several things into account. The silver sub-salt formed by the reducing action of light is not only readily capable of being further reduced by suitable reducing agents, but, since the reaction is essentially a reversible one, in the absence of a sensitizer (gelatine in this case), the sub-salt is quite as readily oxidized again. Thus, silver bromide, sealed up in a glass tube from which the air has been exhausted, when submitted to light is separated into bromine and silver sub-bromide. But as soon as the tube is taken away from the light, bromine and sub-bromide commence to recombine, forming silver bromide again. By experiment with the different regions of the spectrum, it has been shown that the reversing effect is produced by the rays of greater wave-length (*i.e.* from the lower, or red, end of the spectrum). Taking this fact in connection with our experiment in which potassium dichromate prevented the negative image from being formed after a normal exposure, we see that when a plate is exposed for a sufficient length of time, the silver sub-salt formed, so to speak, by the short wave-lengths in the normal part of this exposure is by the action of the longer wave-lengths in the balance of the exposure time caused to unite with oxygen from the air, that is, it is reoxidized. But in the meantime those portions of the silver salt which, after normal exposure, would have remained unreduced to sub-salt, by the excessive exposure have been so reduced. The condition of the plate, consequently, now is such that the portions of silver salt which normally would be reducible by the developer, having been reoxidized, are incapable of reduction; whereas those portions which normally would not have been reducible are present as light-reduced sub-salts and therefore are reduced to silver by the developer. So a reversed image must be formed. By incorporating in the emulsion a suitable reducing agent, which not only prevents the reoxidation of sub-salt, but also serves as absorbent of the greater amounts of bromine set free in prolonged exposures, reversal can be entirely prevented. Plates thus prepared are incapable of forming reversed images even with exposures many hundred times the normal, and thus cannot be overexposed. By this means sufficient exposure can be given to secure details in the shadows without at the same time completely blocking up the highlights. Hydrazine salts are the compounds employed for the purpose, and the plates are called Hydrazine, or Hydra, plates. At first thought it might seem that here is a solution of the whole problem of exposure. Use Hydrazine plates and give plenty of time, thus avoiding the Scylla of underexposure, there being no Charybdis. But the matter is not quite as simple as this. There is such a thing as getting too much detail even in the shadows. As in all over-exposed plates, there is a tendency toward flatness in the Hydrazine plates, so that they must be used with discrimination.

There is one defect inherent in glass plates which we must mention before concluding this chapter. It is present very little in celluloid films, and this fact forms another point of advantage of films over plates. When an interior is to be photographed in which brightly illuminated windows are included in the view, the glass negative always shows much blurring about these highlights. There is so much reduced silver all around the images of the windows as sometimes to obscure their outlines. The same effect is also often produced in out-of-door work when patches of sky show through branches of foliage; and it can even be found in portraiture where the subject is dressed in white. The effect is known as "halation," and has a very simple cause, and an equally simple cure. In the thin coating of emulsion upon the glass plate it is impossible that all of the impinging light should be absorbed. The part that is absorbed by this film performs, as we have seen, its chemical work and produces the latent photographic image. That portion of the light which, failing to be absorbed, is transmitted through the coating passes into the glass behind it. Here again a small part is absorbed by the glass, while the remainder finally reaches the under surface of the plate. At this surface another division occurs, part of the light passing through and into the space behind the plate, and the rest suffering reflection. It is the reflected part of the light, which has come through the sensitive coating and the glass, which produces the untoward effect of halation, for it now is directed back toward the under side of the gelatine film, at an angle such as to strike the film at a different place from where it came through. Passing into the emulsion it, of course, forms sub-salt of silver all around the latent image of the highlight in question. To prevent this reflection at the back surface of the glass is to do away with halation, and there are two methods in use. One is to apply a coat of slow emulsion upon the glass, over which a second rapid film is spread. Such double-coated plates are a great improvement over the single-coated variety in several ways, but while halation is very much diminished by this means, it is not in fact entirely eliminated. The second method is to coat the back of the plate with a substance which will absorb all of the light which reaches that surface of the glass. None can then be reflected to the under side of the emulsion. Such a "backed" plate can be had at a slight extra cost over the unbacked kind, and once used will probably mean always used.

CHAPTER V

CHEMISTRY OF DEVELOPMENT

CHEMICALLY speaking, the development of a negative consists in the complete reduction, to metallic silver, of the light-affected silver salt. In order thus to get a negative, it is necessary, of course, that the unaffected silver salt should escape such reduction. This fact, then, establishes the prime characteristic of a photographic developer, namely, that its reducing power with silver salts must be so adjusted as to enable it to act selectively upon these light-exposed compounds in the emulsion, reducing the sub-salts and leaving unreduced the remaining silver bromide and silver iodide. In our experiments with the strong reducing agent, ferrous sulphate, we learned that its simple solution in water is capable of instantly reducing silver nitrate to silver. But by acidifying the ferrous sulphate, we were able to control and modify its reducing power, even a few drops of acid greatly retarding the reaction, although not preventing it entirely from taking place. Since all chemical action involves energy, *i.e.*, work, it is plain that a certain amount of chemical work must be performed when silver is reduced from such a compound as silver nitrate, or silver bromide. Now, in consequence of the law of conservation of energy, the amount of work done when a given quantity of silver bromide, for example, is completely reduced to silver is the same as the sum of the amounts concerned in the partial reduction of this quantity to sub-bromide and the final reduction of sub-bromide to silver. In other words, it makes no difference in the total quantity of chemical work done whether the reduction be all at once to silver or whether it be carried out in the two steps. Therefore, evidently, since the energy of light has been used in the first step, that is, in the reduction to sub-salt in the exposure, there is less chemical work for the reducing agent in the developer to do in reducing the sub-bromide than in reducing the unaffected silver bromide. This explains why a suitably regulated reducing agent (the photographic developer) is able to bring out upon the plate in metallic silver the latent image produced in the exposure to light. Because less chemical work is required to be done in the reduction of silver sub-bromide to silver than in reducing silver bromide to the metal, the developer proceeds to act first upon the former. That it will in time act also upon the silver bromide we shall later see.

Experiment 18. Make up a 0.5% solution of pyrogallic acid by dissolving 0.1 gram of the solid in 20 cubic centimeters of water, and mix by stirring with a glass rod. Avoid shaking the tube. Pour a few cubic centimeters into a test tube, shake well, and note that there is no darkening of the solution. Add a drop or two of dilute sulphuric acid to the bulk of the solution and mix by stirring. Shake up a little of this solution in a test tube. The color change is slight. In half of the remaining liquid dissolve 0.2 to 0.3 gram of dry sodium sulphite, and in the other half about the same quantity of anhydrous sodium carbonate. Shake up each of these mixtures and observe how rapidly the second turns yellow, whereas the first shows no change.

Pyrogallic acid is an organic compound obtained by heating gallic acid, which is a constituent of gall-nuts and many other vegetable substances such as, for example, tea. It is a strong reducing agent, being itself oxidized in the process to oxalic and acetic acids. Thus, when exposed to the air, its solutions absorb oxygen, just as do solutions of ferrous sulphate, and oxidation of the pyrogallic acid occurs. But this oxidation does not take place so rapidly in a plain solution of pyrogallic acid, or in one containing free sulphuric acid, as it does when the solution is made alkaline as with sodium carbonate. Also when sodium sulphite, which is likewise a reducing agent and oxygen absorber, is present in the solution, the oxidation of pyrogallic acid is hindered, since the absorbed oxygen is used up first in oxidizing the sulphite to sulphate.

Experiment 19. Dissolve 0.5 gram of sodium carbonate (anhydrous) in 10 cubic centimeters of water, add to this 0.1 gram of pyrogallic acid and observe the color immediately developing. Now add to the mixture a few cubic centimeters of a strong solution of sodium sulphite and note that the yellow color is at once bleached, but that after the lapse of sufficient time discoloration again occurs.

In alkaline solution the brown substance formed by oxidation is soluble. It is in the nature of a dye, and is fairly insoluble in water in the absence of alkali. Its dilute solutions are yellow, turning brown when the concentration increases. Plates and films developed with "pyro" sometimes are stained a yellowish brown because after the free alkali has been washed out this brown dye is insoluble in the water. Also, it seems to have a tendency to become a "fast" color in the gelatine similar to other dyes in fabrics.

Experiment 20. Treat with a few drops of sodium sulphite solution a little silver nitrate dissolved in 5 cubic centimeters of water, and note that white silver sulphite is precipitated. No reduction occurs. Next prepare a small quantity of washed silver bromide unexposed to white light. Dissolve a little of this unexposed salt in a test tube with enough ammonium hydroxide, add to it a little pyrogallic acid solution, and observe the immediate blackening of the liquid. This is due to the reduction of silver and to the dark-colored oxidation products of the alkaline pyrogallate.

Thus in alkaline solution, pyrogallic acid is able to effect the complete reduction of even unexposed silver bromide. The essential condition for this reaction is that the silver bromide should be in solution. In the operation the pyrogallic acid is oxidized, and the bromine combines with the alkali to form alkali bromide, in the case mentioned, ammonium bromide. Reactions:

(1) Silver nitrate + Sodium sulphite
= Silver sulphite + Sodium nitrate
(2) Silver bromide + Ammonium hydroxide
= Silver-ammonia bromide + Water
(3) Silver-ammonia bromide + Pyrogallic acid
= Silver + Ammonium bromide + Oxidation products of pyrogallic acid

Experiment 21. Make up a little "pyro" developer, in two solutions, as follows:

1. Sodium sulphite, dry	10 grams
Pyrogallic acid	3 grams
Sulphuric acid (concentrated)	2 drops
Water, to	100 cubic centimeters
2. Sodium carbonate, anhydrous	5 grams
Water, to	100 cubic centimeters

When ready to use this developer, mix the two solutions and dilute to 300 cubic centimeters with water.

For carrying out this experiment take three small-sized dry plates. The first plate is to be given a normal exposure in the camera or under a negative, but should be taken, like the other two, from the package in total darkness when loading it in the plateholder. After exposing this plate, mix the prepared developer solutions and put about equal portions in each of three trays, adding 1 cubic centimeter of a ten per cent. solution of potassium bromide to the second tray. Turn off the red light, and in the dark take out the other two unexposed plates from the box and the one which has been exposed from the plateholder and, as quickly as possible, slip the three plates into the trays, the unexposed two in the first two, the exposed in the third tray. Cover the trays, after which the red light may be turned on again. At intervals for ten to twelve minutes the covers may be lifted and the plates examined.

The unexposed plate in the first tray will begin to show reduction of silver, that is, "fog," in about two minutes, whereas the exposed plate in the third tray will develop without fogging for as much as ten minutes. In the second tray to which has been added the potassium bromide, the unexposed plate remains free from fog for at least as long as the exposed plate. If a fourth plate were to be exposed normally and put into a solution containing pyrogallic acid, sodium sulphite, and acid, without the addition of any of the alkali, we should see that development, otherwise reduction of silver, would be extremely slow. This effect might be expected from the discussion of Experiment 18, recalling that a solution of pyrogallic acid containing mineral acid possesses far less reducing power than one containing free alkali.

In order to make clear what is indicated by the experiment just described, let us consider that in the gelatine emulsion with which the dry plate is coated we have a layer of gelatine, of definite and measurable thickness, in which are embedded minute lumps, spaced with some irregularity, of light-sensitive silver salt. For convenience we will disregard the silver iodide and consider only the bromide, since the action is essentially the same in the case of both. Thus the particles of silver bromide in the body of the gelatine may be likened to plums in a pudding. The structure of the gelatine itself may be compared somewhat to that of a honeycomb if it be imagined first that the comb consists of the same material precisely as the honey, and second, that, instead of the cells of the comb fitting tightly together all round, there are spaces between in places, making in effect tubes or tunnels into and through the mass. It is by means of these infinitesimal passageways that the reducing solution which we call the developer makes its way into the body of the gelatine and thus comes into contact with the silver bromide particles. If we now limit the discussion to a single one of these particles of bromide, we shall see that its microscopic mass is surrounded on all sides by comparatively transparent gelatine, but that it can be reached by water and by substances dissolved in water through the pores in the gelatine. That is, the particle is accessible to both the light and the developer, but is somewhat protected, after all, from the latter. Taking the first plate which was put, unexposed, into developer containing no potassium bromide, let us see what happens to our particle of silver salt. First, let it be noted that, microscopic though it be in size, nevertheless the particle contains a very large number of molecules of silver bromide. As soon as the alkaline pyrogallate solution penetrates through the gelatine envelope and touches the surface of the particle, silver bromide commences to dissolve in the liquid. That is, molecules of silver bromide begin to pass from the solid particle into the liquid. But we have already learned by an experiment that alkaline pyrogallate reduces silver from a solution of silver salt, and therefore it is not surprising to find here that reduction occurs, if we can be assured that any silver bromide, which we have thought of as an insoluble compound, really goes into solution. As a matter of fact, no substance is really insoluble in the absolute sense. Silver bromide, indeed, is soluble to the extent of 0.002 gram in 1,000 cubic centimeters of water, but its solubility can be varied, as we shall presently see, by having other substances too in the solution. So, as the molecules of silver really do go into the liquid one after another, and at once are reduced there, the silver from them is deposited in solid form practically in the spot formerly occupied by the bromide, the bromine is taken up by the liquid, forming sodium bromide in solution, and a corresponding amount of pyrogallic acid is oxidized. In the experiment with the plate we actually found that silver was reduced, and we called it "fogging" of the plate. This chemical "fog," therefore, is simply the reduction of silver from silver salt without any mediation of light, and is bound to take place so soon as silver bromide and alkaline pyrogallate come together in solution.

But, as appeared from the experiment with the second unexposed plate, such reduction can be very much hindered. This plate was put into developer which differed from that in the first tray by containing a small quantity of potassium bromide. Since this was the only difference between the two experiments, the delay in the reduction of silver can have been caused only by the presence of this potassium bromide. Let us see how this reagent acts towards silver bromide in solution.

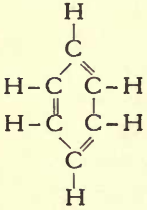
Experiment 22. Dissolve a little silver bromide with a few cubic centimeters of dilute ammonium hydroxide. Add to this solution 2 or 3 cubic centimeters of a fairly strong solution of potassium bromide in water and observe that silver bromide is reprecipitated.

The solubility of silver bromide is therefore less when potassium bromide is present in the solution than in the absence of the latter salt. Thus, when the developer solution containing potassium bromide came in contact with the gelatine-embedded silver bromide particle in the second plate, on account of the diminished solubility of the silver bromide the molecules of this compound were very much hindered in their passing into the solution by the potassium bromide already contained in it. Since the rate at which the silver bromide was going into solution was in this way diminished and since also the rate of its reduction depends upon this rate of solution, it was inevitable, now that we understand the situation, that the reduction, or otherwise the "fogging," should be retarded by the addition of potassium bromide. In photographic parlance this action is called "restraining" action, and potassium bromide, a "restrainer."

Passing finally to the third plate, which was normally exposed, but developed in an unrestrained solution, comparably with the second plate which has just been under discussion, we may perhaps see at once that bromide must have been somehow furnished by the plate, since none was beforehand added to the developer. To explain this circumstance, let us consider again our single bromide of silver particle, enveloped in gelatine, and note what has happened to it during the exposure to light. Let us suppose that the particle was so situated that it received a very intense illumination. Because the energy of the light affecting the particle was great, a correspondingly large number of molecules received such a shaking as to jar loose one atom of bromine from each molecule, and this photo-chemical action was able to penetrate into the body of the particle to a proportionate depth. In the maximum, all the silver bromide molecules of the particle would be in this way reduced to sub-bromide molecules by the light. But as fast as the atoms of bromine were set free, they were immediately taken up by the gelatine, so that, practically speaking, none escaped. Therefore, when the developer solution reached the particle, it found, temporarily combined with the gelatine, a supply of bromine ready at hand with which the sodium carbonate could at once form sodium bromide. This compound, produced right "on the ground," so to speak, where it was most needed, by its restraining effect upon the solubility of any silver bromide in the particle which happened to escape reduction to sub-salt by the light, delayed the reduction of such silver bromide by the alkaline pyrogallate. The action of sodium bromide is exactly similar to that of potassium or any other soluble bromide as a restrainer.

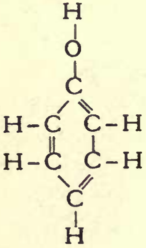
In an area of the plate affected by a weak illumination a much smaller number of bromide of silver molecules will be broken down to sub-bromide, and correspondingly less bromine will be set free, and thus throughout the total extent of the exposed body of emulsion the amount of reduction to sub-bromide will be directly proportional to the intensity of the light. Furthermore, it is important to observe here that the depth in the film of emulsion to which the photo-chemical effect penetrates is dependent directly upon the light intensity. That is to say, in the highlights there is reduction to sub-bromide deeper down in the emulsion than occurs in the shadows. Clearly, in some areas the intensity of the light may be so low that its feeble energy is wholly absorbed in the surface layer of silver bromide particles, while in other regions there will be an excess of energy over the amount absorbable by the whole thickness of the film and consequently some light will be transmitted. Here halation will occur unless the plate is suitably backed. But the silver salt reducible to form an image by the developer is not limited to the light-reduced sub-bromide, for a secondary reaction occurs between the initially reduced silver and the neighboring silver bromide that has escaped partial reduction by light. When a molecule of silver sub-bromide is decomposed into its constituents by the developer, the silver is for the instant left in the atomic condition, the so-called nascent state, in which it is excessively reactive. Nascent silver and silver bromide react together immediately, forming silver sub-bromide, which is reduced by the developer, and in this manner the particle of metallic silver resulting may be much larger than would have been produced merely from the light-reduced salt. So, oftentimes, when it is desired to bring up details in the shadows without at the same time carrying the development of the highlights too far, it is recommended to take the plate from the developer and to allow the action to continue with the amount of solution which has soaked into the emulsion. In the highlights where there is abundance of subbromide, the reducing agent is quickly used up and the action there stops, but in the shadows there is proportionally as much reducer present and fewer subbromide molecules, so that by the secondary reaction just described a considerably greater quantity of silver can be reduced to form an image than would be given merely by the light-reduced salt. Too great stress must not be laid upon this idea of modifying in the development the gradation established by the exposure. It was formerly believed that gradation could be considerably altered by suitably adjusting the developing solution. But it is now known that with a given plate the relations between the densities of the grades are practically determined by the exposure, and can be little affected by the development process. If the ratios of the intensities of three tones as given in the exposure are as 1 : 2 : 3, then in the negative produced the densities will be in the same ratios without regard to the constitution of the developer or to the time of development. By the term "density" is here meant the quantity of silver reduced under definite conditions by the developer. It is possible to stop development at such a point that all three tones are, so to speak, printable, that is, are sufficiently transparent to print; or development can be carried so far, for example, as to make density "3" so opaque that the ratio of transparency between "2" and "3" is quite different from the density ratio of 2 : 3. In such a case the gradation obtained in the print will be quite different from the original intensities of tones. This example will sufficiently indicate, perhaps, that the principal means of modifying or controlling gradation lies in changing the duration of development, and not in varying the composition of the developer. It is upon this principle of Constant Density Ratios that all the various factorial, time, and tank methods of development are based.

So far, in speaking of developing agents, we have referred to them in general terms as organic compounds. Let us examine them a little more closely, in order to find out what these interesting substances are and how they are related to one another. When coal is subjected to distillation for the purpose of making coke and illuminating gas, there is separated as one of the by-products a quantity of tarry material known as coal-tar. The substance, once a waste product, but now the basis of important industries, is fractionally distilled and by this means there is obtained, among other valuable things, the compound benzene (or benzol). When pure, benzene is a colorless liquid, lighter than water, and boiling at 80.5 degrees C. A great many substances which are insoluble in water, such as fats, resins, etc., are soluble in benzene, so that it is much used as a solvent, but still more extensively for the manufacture of the so-called benzene derivatives, among which, in fact, are most of our developing agents. Benzene is an extremely stable compound, consisting only of the two elements carbon and hydrogen. It is with difficulty decomposed, suffering no change when boiled with strong alkali, and only slowly oxidized by such vigorous oxidizers as chromic acid and potassium permanganate. But when suitably treated, benzene very readily yields a large number of what are called substitution products, or derivatives—substances, that is, derived from benzene by substituting a great variety of different elements and combinations of elements in place of some or all of the hydrogen. The percentage composition of benzene is such that, taking into account also the density of its vapor, we know it to consist of six atoms of carbon united with the same number of atoms of hydrogen. Employing the usual chemical symbols, the formula of this compound is consequently written C_6H_6. With so many atoms of two elements there is possible a number of different ways in which these atoms might be joined together, but it is fairly easy to show that one method of representing their arrangement best explains the chemical behavior of the compound. The well-known substance acetylene gas is also a compound of hydrogen and carbon, and with a percentage composition identical with that of benzene. Its vapor density is but one-third as much as the vapor density of benzene, and so its formula is written C_2H_2. But also it can be proved that in acetylene each hydrogen atom is combined to a carbon atom and that the two carbons are tied together, so that this compound is graphically represented thus: $H\text{-}C\equiv C\text{-}H$. Now, if acetylene gas be passed into a tube which is kept at dull red heat, there will emerge from the other end of the tube, not acetylene gas, but the liquid benzene. So three molecules of acetylene are in this way combined together to form one molecule of benzene, $3\ C_2H_2 = C_6H_6$, and such a reaction is known chemically as polymerization. Since in acetylene each hydrogen atom is joined to a carbon atom, it is reasonable to suppose that in benzene, the polymer of acetylene, the same arrangement holds true. Therefore the arrangement of the atoms in benzene, or its "constitution," to use the chemical term, is considered to be representable graphically as shown in the margins.



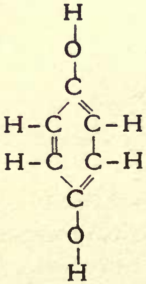
Benzene

The six carbons are all joined together in a ring (this forms the so-called "benzene ring") and each has a hydrogen atom attached. If we suppose that the ring is difficult to break apart chemically, but, on the other hand, that the hydrogen atoms can easily be taken off and replaced by other elements and groups of elements, we shall see that this ring formula very well represents the chemical facts which we have previously stated about the compound.



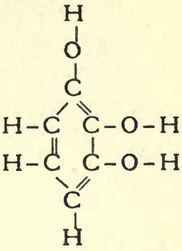
Phenol

When one hydrogen is taken off and in its place is put -O-H, we have the compound phenol, or carbolic acid, a crystalline solid. Such an action illustrates the formation of "substitution products" or benzene "derivatives." If we also make a similar substitution of -O-H on the opposite side of the ring, we get the well known developing agent hydrochinon, or paradihydroxybenzene. By substituting three -O-H's on three adjacent carbon atoms in the ring, there is formed 1, 2, 3, trihydroxybenzene, the photographer's good old stand-by, pyrogallic acid, "pyro" for short.



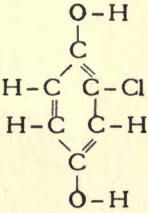
Hydrochinon

With proper treatment chemically, hydrochinon, which as a developer gives excellent density but has a tendency to "hardness" and lack of details in the shadows, can be converted into adurol, a more rapid developer, giving better detail, and one that keeps better in solution than the hydrochinon from which it may be derived. Adurol is monochlorhydrochinon, or, as made by another manufacturer, monobromhydrochinon.

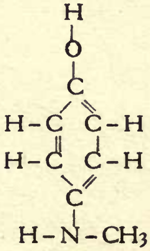


Pyro

As examples in another series of substitution products may be given the developers amidol and metol. These are both substituted phenols. Metol chemically is monomethylparamidophenol. Amidol is diamidophenol, and ortol is hydrochinon combined with monomethylorthoamidophenol.

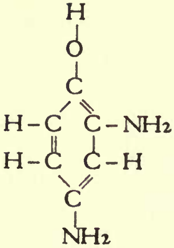


Adurol

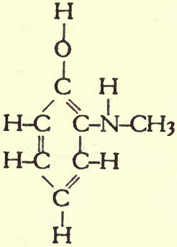


Metol

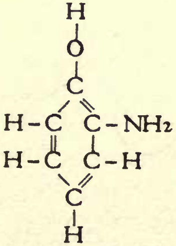
If we particularly note these seemingly awkward chemical names of photographic developers, we find in many of them the prefix "para," and in others "ortho." These prefixes, together with a third, "meta," are used to signify which of the hydrogen atoms, as related to a given hydrogen, have been replaced. Thus, if two adjacent hydrogens are substituted, as by -O-H and $-NH_2$, orthoamidophenol is produced, but if instead the first and third hydrogens are replaced, the compound



Amidol



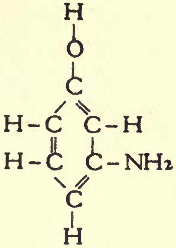
Ortol



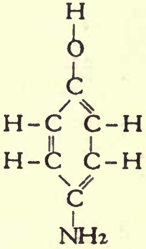
Orthoamidophenol

is metamidophenol, and if the substitutions are on the first and fourth carbon atoms, paramidophenol results.

These three compounds can actually be prepared, and that they are different substances, although possessing the same composition, is attested by the fact they have different properties. The difference is in their constitution. A very peculiar circumstance about the series of benzene derivatives is that, whereas the ortho- and para-compounds possess the power of developing the latent photographic image, the corresponding meta-compounds do not have this power. Also, in general, developing power is increased by increased substitution. As an example of this is the case of adurol already mentioned, which is a more active developer than hydrochinon, and yet differs from it in composition and constitution only in having another hydrogen atom replaced by an atom of chlorine. Recalling that in amidol developing solutions no alkali is included and referring to the graphic formulas for metol and amidol just given, we see that it is the third substitution on the ring which gives to amidol so much greater developing power than is possessed by metol. Amidol is so vigorous a reducer that its solution is used for development simply with the addition of sodium sulphite. If even a few drops of alkali solution are added, fog is likely to supervene, on account of the general reduction of silver bromide all over the plate.



Metamidophenol



Paramidophenol

A comparison of all the developing agents in the market will show advantages and disadvantages for the amateur. Some produce excellent negatives, but their solutions do not keep well; others have poisonous properties besides, as for example, metol. Still others, like pyro, are prone to stain the gelatine. Some are rapid; and some work slowly. Perhaps it would be difficult to say whether pyro or metol-hydrochinon is the more used developer, but one or the other of these is probably the most widely used of all. It would be about equally difficult to explain why these two developers should be so popular, since neither keeps well in solution, one stains badly and the other is poisonous. Of course, the merits and demerits of developers, like so many other things, are largely matters of opinion. But, nevertheless, there are developing agents which keep well in solution, do not stain the film, and are not especially poisonous; which also, in reality, produce quite as excellent gradation as pyro, for example, work with as much rapidity as metol, and are no more expensive. One such developer is the duratol-hydrochinon, formulas for which have been extensively published. It is particularly to be recommended to the amateur since it keeps well, almost indefinitely, in fact; and the same solution can be used for plates, films, papers, and lantern slides, by merely varying the dilution. Standard recipes for developers will be found in the Appendix.

CHAPTER VI

CHEMISTRY OF THE FIXING PROCESS

WHEN the operation of transforming the latent photographic image into reduced metallic silver has been completed, according to the judgment of the photographer, the gelatine film upon the plate contains a considerable number of different substances. To enumerate them, there is first the silver which is to form the negative; besides this, there is also the unreduced remainder of the unexposed silver bromide and silver iodide, and in addition to these, the gelatine is, like a sponge, saturated with the solution of all the soluble materials which the developer now holds. These last include the unoxidized reducer, the alkali, the sulphite, sodium bromide, and sodium iodide, and the oxidation products of the developing agent used up, some of which may possess the character of dyes. In order to make a permanent negative out of this combination, it is necessary that everything be removed so far as it is possible except the metallic silver and the gelatine. Upon taking the plate from the developer solution, the greater part of the soluble materials clinging to the gelatine should be washed away by rinsing liberally with water. But primarily it is required to get rid of the silver salt which is still light-sensitive, and the means for doing this must now be discussed. By recalling experiments already performed, we remember that silver chloride and silver bromide are soluble in ammonium hydroxide. Silver iodide is very insoluble, but this reagent has another disadvantage which is serious, namely, that it has a bad effect upon the gelatine. This is the reason why ammonium hydroxide is no longer much used as the alkali in developer solutions. Another compound whose solution in water is capable of dissolving all three of the silver halogen salts is potassium cyanide. But, although very extensively used in metallurgical industry for the extraction of gold and silver from their ores, potassium cyanide, on account of its extremely poisonous character, is not a reagent that can safely be recommended to the photographer.

Experiment 23. Prepare small amounts of silver chloride, silver bromide, and silver iodide and treat each of them with a few cubic centimeters of a strong solution of sodium thiosulphate (the "hypo" of the photographer), noting the solvent effect in each case. Also to a little cold, dilute sodium thiosulphate solution add a drop or two of silver nitrate in solution and note that the silver thiosulphate at first precipitated is white.

The color changes are due to the fact that silver thiosulphate decomposes and ultimately forms black silver sulphide. This can be shown by heating the mixture. If an excess of the thiosulphate is added quickly to a solution of silver nitrate, the precipitate of silver thiosulphate at first formed is at once dissolved, producing silver-sodium thiosulphate, which is the same soluble compound that is formed by treating silver chloride with thiosulphate. Reactions:

(1) Silver bromide + Sodium thiosulphate
= Silver-sodium thiosulphate + Sodium bromide
(2) Silver nitrate + Sodium thiosulphate
= Silver thiosulphate + Sodium nitrate
(3) Silver thiosulphate
= Silver sulphide + Oxygen + Sulphur dioxide
(4) Silver thiosulphate + Sodium thiosulphate
= Silver-sodium thiosulphate

Although the unreduced silver salt remaining after development has been completed is still sensitive to light, it is by no means as sensitive as it was before development. If, when it is judged that enough silver has been reduced, the plate is well rinsed in two or three changes of water, the unaffected silver salt is so little sensitive that it can be exposed for a short time to the weak illumination of an ordinary room without damage. Of course it must not be handled in a strong light. This is why in the tank development of roll film it is possible to remove the film from the tank and place it in the fixing bath without resorting to a darkroom. But although the sensitiveness is so much lessened, nevertheless to make the negative permanent it is necessary, as has been remarked, to take away from the gelatine everything possible but the silver. Thus the "fixing" process in reality is a twofold operation, since it consists in making the insoluble silver bromide and silver iodide over into soluble silver-sodium thiosulphate by means of the action of the "hypo" of the so-called "fixing bath," and afterwards washing out of the gelatine all the soluble salts which it contains. Ideally, a negative should consist solely of pure silver particles embedded in clean gelatine. The more nearly this condition is approached the better the chemical quality of the negative. In practice it is not so simple a matter to effect this desirable state of things. Some of the soluble substances contained in the gelatine appear to "fix" themselves there somewhat as dyes are fixed in fabrics, in part, perhaps, adhering to the silver image. Certainly, at least, the staining matter from the developer solution is in some way retained by this image, as can be ascertained by treating such a discolored negative with nitric acid. In this manner the silver will be dissolved out, and the stain, being insoluble in acid (although it forms soluble products with alkali), remains in the film, in fact forming, as it were, an image made of this dye-like substance. It has been claimed that the reduced silver holds fast some of the unreduced silver bromide, refusing to give it up even to the thiosulphate. Whether or not this be true, if the decantation process of washing precipitates is recalled to mind, it will be evident that here also the soluble materials can be washed away from the insoluble to any desired extent, but never quite entirely removed. It is possible and often desirable to make chemical tests of the wash-water in order to determine the degree to which the soluble thiosulphate has been eliminated from the plate. The reaction between silver nitrate and sodium thiosulphate already mentioned can be utilized for this purpose.

Experiment 24. Make up a 1.0 per cent. sodium thiosulphate solution by dissolving 1.57 gram of the solid in a little water and diluting up to 100 cubic centimeters with water. Mix this solution thoroughly. Make a 0.1 per cent. solution by diluting 10.0 cubic centimeters of the 1.0 per cent. solution to 100 cubic centimeters; and lastly a 0.01 per cent. solution by diluting 1.0 cubic centimeter of 1.0 per cent. to 100 cubic centimeters. Take 10 cubic centimeters of each of these three solutions, warm, and add to each one drop of silver nitrate in dilute solution. Even the third solution, containing so little thiosulphate as one part in ten thousand, gives a perceptible black precipitate of silver sulphide. If the most dilute of these solutions be still further diluted, the precipitate will be yellowish instead of black, but will be distinct. Thus this reaction furnishes a method of detecting very small amounts of thiosulphate. Reaction:

Sodium thiosulphate (heated) + Silver nitrate
= Silver sulphide + Silver sulphate + Sodium nitrate
+ Sulphur dioxide + Sulphur

In utilizing the reaction of the preceding experiment for testing the thoroughness of the washing, a plate may be taken out of the washing tank and the water allowed to drain from one corner into a test tube until 5 to 10 cubic centimeters have been collected. This water is next warmed, and then a drop of silver nitrate solution is added. If even the faintest darkening occurs, washing should be continued. However, we may remark that if the water used for washing contains more than a very small amount of soluble chlorides, the addition of silver nitrate will precipitate white silver chloride, which will interfere somewhat with the delicacy of this test. In such a case use may be made of another reaction, as in the following experiment.

Experiment 25. Prepare a solution as follows: In 100 to 150 cubic centimeters of distilled water dissolve 1.0 gram of potassium carbonate (anhydrous) and 0.1 gram of potassium permanganate. Dilute to 1,000 cubic centimeters with distilled water. Treat 10 cubic centimeters of each of the three solutions of thiosulphate made up in the previous experiment with 2 or 3 drops of this alkaline permanganate solution. The mixture will have a green color, or blue, if the thiosulphate is very dilute. Reaction:

Potassium permanganate (Pink)
+ Potassium carbonate + Sodium thiosulphate
= Potassium manganate (Green) + Sodium sulphate
+ Potassium sulphate + Carbon dioxide

This solution may be kept in a bottle for the purpose of testing the wash-water from plates, films, and papers. Although it may seem an unnecessary complication to take the time to test the completeness of washing, when by merely allowing the water to run long enough negatives or prints may be considered free from soluble substances, there are in reality sufficient benefits derived from making this test to warrant the photographer in adopting it as a part of his regular procedure. If he knows from actual experiment that the quantity of thiosulphate ("hypo") remaining in his negatives is less than a definite very minute amount (and so for practical purposes a harmless amount), he will never have the unhappy experience of beholding the crystallization of salts upon his plates, which not infrequently befalls the amateur who takes for granted the thoroughness of his work. And besides this, there is nothing to be gained, leaving out of account the waste of water, and very often considerable damage, especially to papers, by unnecessarily prolonged soaking. As we have repeatedly observed, the essentials of photographic processes are chemical in their nature, and since one is never safe in taking things for granted in regard to the results of chemical operations, it may be laid down as axiomatic that the particular worker, the photographer who makes a practice of taking pains and precautions in his chemical work, will produce the most technically successful negatives and prints. In this connection there is a point which should not be lost sight of, namely, that no amount of washing can be expected to take away insoluble substances. It is necessary in the first instance to allow the "hypo" to act upon the silver bromide and silver iodide for a sufficient time so that the conversion of these water-insoluble substances into the water-soluble double thiosulphate of silver and sodium may be effected completely. By allowing the plate to stay in the fixing bath for at least ten minutes after the creamy silver halogen salts have disappeared, one can always be assured of thorough "fixing," provided the thiosulphate solution is reasonably fresh, and not approaching exhaustion. Much of the amateur's trouble in the way of poor negatives and prints is doubtless traceable to the overworking of the fixing solution, not to say also of the developer. It may be that a supply of developing solution and a stock of "hypo" will last for a greater length of time measured in months, and will develop and fix more negatives, if used until the last vestiges of chemical activity have been exhausted, but such a proceeding is not conducive to excellence and uniformity and permanence of results. Neither is such a method really economical, for the saving in developer and "hypo" is far overbalanced by waste of the much more expensive plates, films, and papers that are spoiled. The best practice for the amateur to adopt is first never to use over again a solution which has once developed a plate or film, and second to mix enough fresh, plain thiosulphate "fixing bath" for each batch of plates or films, throwing it away when they are done. There is no better fixing solution for plates and films than plain "hypo," if one of the non-staining modern developing agents has been used. Besides this, if a tendency to discoloration appears, the stain can be bleached by adding a little sodium sulphite, or, even better, the potassium disulphite which is commonly called "metabisulphite."

The "acid" fixing bath is simply a solution of "hypo" to which is added sulphite and enough acid to liberate some sulphurous acid from the sulphite, but not sufficient to decompose the thiosulphate. Recalling the use of sodium sulphite and potassium metabisulphite in developing solutions where they are commonly called "preservatives," we may remember that their function is equally to prevent the formation of dyes which would produce discoloration. So in this sense they are "bleachers." In the fixing bath they perform the same service, preventing the gelatine from becoming discolored by bleaching the dye which has been formed in the developer. It is in fact the sulphur dioxide, or sulphurous acid, as the solution of this gas in water is called, which is the effective bleaching agent. The acid used to set free the sulphurous acid from sodium sulphite is ordinarily citric or tartaric acid, but sometimes very dilute sulphuric acid is employed. The reactions are as follows:

Sodium sulphite + Citric acid
= Sulphurous acid + Sodium citrate
Sodium sulphite + Sulphuric acid
= Sulphurous acid + Sodium sulphate

Sulphurous acid is a very unstable compound and is known as such only in solution. Even there it is continually breaking down into its constituents, sulphur dioxide gas and water, and this is the reason why its solutions have such a pungent odor. Like its sodium salt it is a reducing agent, and it is upon this fact that its efficiency in preventing stain depends. All dyes, on becoming reduced, form colorless products, and it is this action which is called bleaching. Potassium metabisulphite, or "disulphite" as it really should be named, produces similar results by reason of the fact that its solution is, in effect, the same as a sulphite solution to which acid has been added. This compound is, as it were, potassium sulphite containing extra sulphur dioxide which it easily gives up. Therefore, to recapitulate, the addition of acid to sodium or potassium sulphite, or to disulphite, produces the sodium or potassium salt of that acid and sulphurous acid, if the action goes on in solution. But, as we have said, sulphurous acid spontaneously decomposes into water and sulphur dioxide, so that the reaction given above might be written quite as well:

Sodium sulphite + Sulphuric acid
= Sulphur dioxide + Water + Sodium sulphate

Next we must inquire into the effect of acid upon sodium thiosulphate.

Experiment 26. Add a little dilute sulphuric acid to 5 cubic centimeters of a fairly concentrated solution of sodium thiosulphate, note the yellowish-white precipitate, which is sulphur, and cautiously smell the odor of the sulphur dioxide gas which is given off. Try the effect of the same acid on more dilute thiosulphate solutions, and observe that similar results follow. Dissolve a crystal or two of citric acid in water and try the effect of its dilute solution upon thiosulphate. Similarly experiment with dilute acetic acid, observing that with these so-called organic acids also the separation of sulphur and evolution of sulphur dioxide occur. Reactions:

1. Sodium thiosulphate + Sulphuric acid
= Sodium sulphate + Sulphur + Sulphur dioxide
+ Water
2. Sodium thiosulphate + Citric acid
= Sodium citrate + Sulphur + Sulphur dioxide
+ Water
3. Sodium thiosulphate + Acetic acid
= Sodium acetate + Sulphur + Sulphur dioxide
+ Water

Next dissolve 0.2 or 0.3 gram of sodium sulphite in about 5 cubic centimeters of water and add several drops of dilute sulphuric acid, avoiding an excess of the acid. This solution will now contain, referring to the reaction above, sodium sulphate and sulphurous acid, besides sodium sulphite, since the last-named compound is in excess. Treat a little thiosulphate in solution with some of this sulphurous acid and note that there is no deposition of sulphur.

Since the sulphur set free, when thiosulphate is acidified, comes from the spontaneous decomposition of the thiosulphuric acid formed, it is plain that sulphurous acid is unable to react with sodium thiosulphate to liberate thiosulphuric acid. Therefore if we make a mixture of sodium sulphite and thiosulphate in the same solution and add to it a less amount of acid than would be equivalent to the sulphite, we should expect the acid to interact with the sulphite, forming sulphurous acid in the solution, and, since in this way the danger of forming thiosulphuric acid is removed, there should be no separation of sulphur. An experiment will show that this is the case, and it is in such a manner that the "acid" fixing baths are made up. Whenever sulphur is precipitated from such a bath, it is evidence of the presence in the solution of some free acid other than sulphurous acid. It is this separation of sulphur from thiosulphate which is one of the causes of lack of permanency in negatives and prints that have been imperfectly washed, so that any agency which is capable of decomposing thiosulphate should be used in photographic solutions with care and intelligence. For the making of negatives, at least, except possibly in very hot weather or in the tropics, there is no fixing bath better than one of plain "hypo," to reiterate a statement already made. At most there need be added to this nothing more than a little potassium metabisulphite. If there is real danger that the gelatine will become too much softened, then a hardening agent should be employed in an acid "hypo" bath. One of the best of these is the "acid fixing and hardening bath" which has been recommended for a long time past with Cramer plates. The hardening consists in rendering the gelatine more insoluble in water and for this purpose a chromium salt is used, generally "chrome alum," or, chemically, potassium chromium sulphate. By treatment with chrome alum the solubility of gelatine is very greatly diminished, so much so that after a sufficiently prolonged application the plate can be washed even with hot water without danger of melting. There is no special advantage in hardening the film to such an extent, but on the other hand it will be distinctly disadvantageous if any after-treatment is to be used. Another disadvantage of the acid fixing bath is that it is often liable to be used after its efficiency has become too much impaired. For a plain "hypo" fixing bath for general use, dissolve 100 grams of the crystallized salt in enough warm water and dilute to 500 cubic centimeters. Since sodium thiosulphate crystallizes with 5 molecules of water, this will make a solution a little stronger than 12 per cent. in sodium thiosulphate. This is for fixing plates and films; for prints, use 75 grams, instead of 100 grams, of "hypo," and 12.5 grams of potassium disulphite (metabisulphite). The same amount of the latter compound can be added to the bath for plates also.

There has at various times been suggested a number of "hypo eliminators," but none of them is to be recommended on account of the lack of permanency in the negatives so prepared. They all work upon the same principle, the oxidation of thiosulphate either to tetrathionate or to sulphate. Among these oxidizing agents are hypochlorites, hydrogen dioxide, potassium permanganate, percarbonates and persulphates. It is quite as easy to wash soluble thiosulphate out of the gelatine as any other soluble products, and no "hypo eliminator" can eliminate the process of washing, so that there seems little to be gained by adding an extra operation to the chemical processes of the photographic art.

After the removal of all dissolved materials from the gelatine film, the last step in the making of a negative, unless some modifications are to be made upon it, is the drying out of the water. The plates may be set in a drying rack and put in a cool, airy place until completely dried. The drying-room should be as free as may be from dust, and there ought to be no considerable change in temperature during the drying. The more rapidly drying takes place, therefore, the safer for the negatives. When a plate dries slowly until partly done and then, with a wet patch in the middle, is finished at a different temperature, there may be a marked difference between the density of the portion that dried at the one temperature and that which dried at the other. In this way the printing quality of the negative will be spoiled. A mistake which is common in many plate-racks is that the grooves are too close together. Plates are brought so near to each other that free circulation of air between them is impeded and uniform drying is rendered difficult. The least distance which it is advisable to have between the plates is about one inch. A rapid method of drying which has been devised is to immerse the plate in a very concentrated solution of sodium or potassium carbonate. Such a solution has a strong affinity for water, so that the water in the gelatine is at once seized by the sodium or potassium carbonate, and in a short time the plate can be removed from the bath quite dry. The process must be used with care, however, as the film sometimes leaves the glass. It must not be used with films, which will be ruined by distortion. When it is desired to dry a negative rapidly, it may, after draining for a few minutes, be placed in a tray containing ordinary alcohol. An immersion of 5 to 10 minutes allows the water in the gelatine to become mixed by diffusion with alcohol, and thus largely replaced by the alcohol, after which the negative will dry very quickly owing to the rapid evaporation.

Upon the skill with which the principles we have so far considered are applied depends the success of the photographer, whether he be specially interested in straight record photography or in pictorial work. Although it is at the same time true that the negative is merely the means to an end, viz., the print, nevertheless it is in the wonderfully modulated silver deposits of the negative that are recorded the gradations of light and shade of which the object depicted, speaking photographically, consists. No matter what modifications may be later introduced in the print to suit the desires and taste of the worker, the basis of all good photography of whatever sort is careful attention to the psychological, optical, and chemical laws, which, when understandingly obeyed, make the negative a truthful and yet flexible medium between the object photographed and the picture which is finally obtained. For this reason the reader is urged, if he wishes to secure the greatest pleasure and benefit from his excursions in the photographic realm, to pay particular heed to his chemical work. The cultivation of accurate and intelligent methods in field, studio, and darkroom will lead even the tyro farther into the "mysteries" than he may anticipate.

CHAPTER VII

AFTER-TREATMENT OF THE NEGATIVE

WHEN the exposure of the plate, upon an object whose range of gradation is not too great, has been confined within the limits of the latitude of the emulsion, and its development has been carried out to the proper degree of opacity, nothing remains but to select such a printing medium as will give the effects desired in the finished picture. But more or less frequently it will happen that these ideal conditions will not all be fulfilled. Either the original contrasts of the object photographed were too great, or under- or over-exposure has been given, or sometimes the duration of development is not properly regulated. If the divergence from these normal conditions is more than a comparatively moderate amount, there is no better advice to give the photographer than to make another trial and use greater care. Not always, of course, can the exposure be repeated, and when this is the case, if a print must be had, it is possible to modify the negative to a considerable extent by the processes of intensification and (as it is called) reduction. In general, both kinds of operation consist in the beginning of the same type of reaction, namely, the oxidation of a part of the silver of which the image is composed.

Some intensification methods do not follow this rule, consisting, instead, of the suitably-controlled reduction of silver from the solution applied to the plate. Let us consider first the mercury intensifiers.

Experiment 27. Give a brief exposure to each of three small plates and develop, fix, and wash them as usual. Make up 100 cubic centimeters of a two per cent. or three per cent. solution of mercuric chloride ("corrosive sublimate," a violent poison and antiseptic). Immerse one end of each prepared negative in this solution until completely bleached, observing the change from the back by transmitted light. Wash the three plates thoroughly for ten to fifteen minutes and then treat them severally as follows. Take 50 cubic centimeters of water in a small tray, add a few drops of ammonium hydroxide, and put one of the plates into this solution. An immediate blackening of the bleached image will be noted. Dissolve 5 grams of sodium thiosulphate in 25 to 30 cubic centimeters of water, dilute to 50 and treat the second bleached plate with this solution. Here again will occur a darkening of the whitened portion. To blacken the third plate, use a regular developer solution. The three plates may now be well washed and dried, and the opacities of the intensified and unintensified parts compared.

In explaining the chemical reactions which take place in this operation, we may first observe that there are two classes of mercury compounds representing two conditions of oxidation, namely, the mercuric salts, the higher condition, and the mercurous, the lower. Mercuric salts can be changed, by the action of reducing agents, to mercurous; and *vice versa,* the mercurous are oxidizable to mercuric compounds. Further, mercurous compounds are completely reducible to elementary mercury, and, when this reduction takes place from a solution of the mercury salt, the resulting mercury is in a very finely divided condition, and, since its absorption of all wave-lengths of light is very complete, its color is an intense black. Now, as we saw in the chapter on the photo-chemistry of silver salts, the silver of which the negative image consists is also in a fine state of division, and in this condition is a good reducing agent. Consequently, when mercuric chloride solution is applied to the negative, the silver reduces an equivalent amount of the mercuric chloride to mercurous chloride and is at the same time itself oxidized to silver chloride. Thus the bleached image consists of a mixture of equivalent quantities of silver chloride and mercurous chloride, both being insoluble white substances. There may also be some unchanged silver. Reaction:

Silver + Mercuric chloride
= Silver chloride + Mercurous chloride

The character of the mercury compound will be seen from

Experiment 28. Prepare a few cubic centimeters of sodium sulphite solution, acidify with a drop or two of dilute sulphuric acid, and add to it about 10 cubic centimeters of two per cent. mercuric chloride solution, observing the white precipitate of mercurous chloride, which is formed by the reduction of the mercuric salt. (If the mixture were now to be heated, mercurous chloride would be further reduced to elementary mercury, but this is not desirable in the present experiment). Allow the mercurous chloride to settle, wash it by decantation, and keep it for use in a subsequent experiment. Reactions:

(1) Sodium sulphite + Sulphuric acid
= Sulphurous acid + Sodium sulphate
(2) Mercuric chloride + Sulphurous acid + Water
= Mercurous chloride + Sulphuric acid + Hydrochloric acid

Now, of the three bleached plates the first was treated with diluted ammonium hydroxide. That is to say, the mixture of silver and mercurous chlorides was acted upon by the ammonium hydroxide in such a way as to form a black product. By reference to the behavior of silver chloride with ammonium hydroxide, we remember that a soluble product is formed, the reaction being thus:

Silver chloride + Ammonium hydroxide
= Silver-ammonia chloride + Water

The action of ammonium hydroxide upon mercurous chloride may be shown as follows:

Experiment 29. Take a portion of the mercurous chloride prepared in Experiment 27 and treat it with a few drops of dilute ammonium hydroxide, observing the instant blackening which occurs. There are formed as insoluble products in this reaction elementary mercury, which is black in a fine state of division, and mercury-ammonium chloride, which is white. Reaction:

Mercurous chloride + Ammonium hydroxide
= Mercury + Mercury-ammonium chloride + Ammonium chloride + Water

The mixture of these black and white insoluble substances is black. Thus in this first process of intensification, the silver image is changed initially to one composed of silver, silver chloride, and mercurous chloride. By the ammonium hydroxide the silver chloride is rendered soluble and the mercurous chloride is converted to an insoluble black mixture of mercury and a complex mercury compound. So, when the first plate is finally washed, the image remaining consists of silver and mercury, plus the small amount of white complex substance. The color of the intensified image formed in this way is generally a dark brown, which makes the process, when successfully carried out, suitable for securing good prints from the negative, but the method has the disadvantage of being somewhat uncertain in its results.

In the case of the second plate with which we have experimented, the mixture of silver and mercurous chlorides was acted upon by sodium thiosulphate. Here again it becomes immediately clear that silver will be removed from the image, since silver chloride and sodium thiosulphate form soluble silver-sodium thiosulphate, carried away in the wash-water. Reaction:

Silver chloride + Sodium thiosulphate
= Silver-sodium thiosulphate

As for the action of the sodium thiosulphate upon mercurous chloride, we already know that not only is thiosulphate a mild reducing agent, but that mercurous chloride is an oxidizer, and therefore the result of their interaction will be to form elementary mercury by the reduction of the one and an oxidation product of the other, thus:

Mercurous chloride + Sodium thiosulphate
= Mercury + Sodium chloride + Sodium tetrathionate

Therefore, in the second method also, by use of "hypo," a portion of the silver image is removed, but is at the same time replaced by a larger quantity of black mercury. This removal of silver from the image is avoided in the third method in which developer solution is used, as the organic reducer acts upon both the silver chloride and the mercurous chloride, reducing them to elementary silver and elementary mercury respectively. Another method of intensification, whereby mercury is added to the silver, consists in treating the plate with a solution containing mercuric iodide and concentrated sodium sulphite. Here silver is oxidized to silver iodide, while mercuric iodide is reduced to the mercurous salt, but immediately the last is reduced by the sodium sulphite to mercury. The plate is then treated with a developer, by which silver iodide is reduced to silver. If this last step is omitted, the intensified image is liable to fade. Reactions:

(1) Silver + Mercuric iodide
= Silver iodide + Mercurous iodide
(2) Mercurous iodide + Sodium sulphite + Water
= Mercury + Sodium sulphate + Hydriodic acid
(3) Silver iodide + Organic reducer
= Silver + Oxidation products of organic reducer

An intensification process in which metallic silver is added to the silver image is one which is known as the "Wellington intensifier." In this a solution containing silver, an organic reducing agent, and an alkali is so adjusted that it is just on the point of precipitating elementary silver. Under these circumstances, when the solution is applied to a negative, the particles of silver already composing the image act as nuclei upon which the silver reducing from the solution can deposit. Thus the image can be built up to any extent desired. This action can be illustrated by taking a little saturated solution, for example, of copper sulphate ("blue vitriol"), putting into it a small crystal of the same substance, and allowing crystallization to take place slowly. The introduced crystal will gradually increase in size, and possibly no other crystals will form, at least for a time. It is easier, so to say, for the copper sulphate in the solution to separate out upon an already formed crystal than to start new ones. In a similar way, it is also easier for the silver separating by reduction from the intensifying solution to deposit upon the silver particles already present in the gelatine than to commence the formation of new particles. To experiment with this process, make up the following solutions:

1.	Ammonium sulphocyanide	4.0 grams
	Sodium thiosulphate.....	4.0 grams
	Water, to...............	25.0 cubic centimeters
2.	Silver nitrate............	2.5 grams
	Water, to...............	25.0 cubic centimeters

Take 15 cubic centimeters of Solution 1 and add to it slowly and stirring constantly 15 cubic centimeters of the second. The action of a silver solution upon ammonium sulphocyanide is, as may be quickly ascertained by experiment, to precipitate white silver sulphocyanide. But in the presence of sodium thiosulphate this precipitation is prevented, owing to the formation of the soluble silver-sodium thiosulphate, until the quantity of thiosulphate present has been used up, when immediately silver sulphocyanide will commence to come down. Reaction:

Silver nitrate + Ammonium sulphocyanide
= Silver sulphocyanide + Ammonium nitrate

If a permanent precipitate is formed by the mixture of the two solutions, add cautiously, a few drops at a time, more of the first until the precipitate is just dissolved. If, on the other hand, no precipitate has been formed, add more silver nitrate carefully until a slight permanent precipitate appears and then barely dissolve it with a drop or two of Number 1. Next dissolve in 2 cubic centimeters of water 0.4 gram of sodium sulphite and 0.2 gram of pyrogallic acid, add 2 cubic centimeters of a ten per cent. solution of ammonium hydroxide, and pour this mixture into the liquid already prepared. Put a dry negative that needs intensification into a clean tray and cover it with this solution, rocking the tray until sufficient density has been obtained. Then put the plate into a fresh fixing bath for five minutes, wash thoroughly, and dry it. In explaining the chemical reaction of this process, we may assume that we have silver sulphocyanide in solution mixed with the organic reducing agent and in contact with the metallic silver of the image. Under these circumstances the silver, which is gradually reduced, deposits upon the metal in the gelatine and not elsewhere, and so there results a building up of the image by an accumulation of silver. Reaction:

Silver sulphocyanide + Pyrogallic acid + Water
= Silver + Sulphocyanic acid + Acetic acid
+ Oxalic acid

There are two other methods of increasing the opacity of negatives which are much employed, one using uranium and the other, chromium salts. The uranium intensifier has the advantage that the operation can be carried on in a single solution, after which the plate must be thoroughly washed, but the negative must in the first instance have been very completely freed from thiosulphate, else the intensification will not be uniform and stains will appear.

Experiment 30. Mix a few cubic centimeters of very dilute solutions of potassium ferrocyanide and uranium nitrate and observe the blood-red coloration that is developed. Uranium ferrocyanide is formed. Compare Experiment 8. Reaction:

Uranium nitrate + Potassium ferrocyanide
= Uranium ferrocyanide + Potassium nitrate

The solution used in this process contains, in addition to the uranium nitrate, potassium ferricyanide acidified with acetic acid. The latter salt, in the presence of the acid, is an oxidizing agent, and thus, when applied to the silver image, oxidizes silver to silver oxide, which with the excess of acetic acid forms silver acetate. But the ferricyanide is simultaneously reduced to ferrocyanide, whereupon there occurs the reaction just mentioned in which insoluble red uranium ferrocyanide is produced. Therefore some of the silver, in being oxidized, is rendered soluble and taken away, but is replaced by the very non-actinic and insoluble uranium compound. Reactions:

(1) Potassium ferricyanide + Acetic acid
= Ferricyanic acid + Potassium acetate
(2) Silver + Ferricyanic acid + Water
= Silver oxide + Ferrocyanic acid
(3) Silver oxide + Acetic acid
= Silver acetate + Water
(4) Uranium nitrate + Ferrocyanic acid
= Uranium ferrocyanide + Nitric acid

To prepare the uranium intensifier, make equal quantities, say 100 cubic centimeters each, of a one per cent. solution of uranium nitrate, and of one per cent. potassium ferricyanide solution containing twenty per cent. of acetic acid (glacial). These two solutions are to be united and may then be used as desired. If by leaving the plate too long in this intensifier the opacity is too much increased, it may be diminished somewhat by long washing in running water, especially if the water be hard. Ordinarily the intensified negative should be washed for about 10 minutes.

The chromium intensifier is one of the simplest to use, in addition to which the operation can be repeated as often as desired. For these reasons it is perhaps more satisfactory than any other method, particularly for the beginner, if he uses the "tabloid" chromium intensifier, which is especially convenient. The plate is bleached in a solution of one of the tabloids, it is washed for a quarter of an hour, and it is then redeveloped in the usual developing solution, the whole operation proceeding in daylight. Solutions for this method may be prepared as follows:

1. Potassium dichromate	5.5 grams
Water, to	100 cubic centimeters
2. Hydrochloric acid (concentrated)	5.5 cubic centimeters
Water, to	100 cubic centimeters

For use take one part of Number 1, one part of Number 2, and two parts of water. This mixture does not keep well, and should be made only as it is to be used. If the plate is dry, it must be soaked in water for an hour. Leave it in the chromium solution until bleaching is completed, wash it free from all chromic acid, expose it to daylight for a few minutes, and then redevelop it, best in a developing solution suited to bromide paper. Finally wash thoroughly. By this process the printing value of a negative may be increased to one and one-half times its original printing value.

When a dichromate solution is acidified, chromic acid is liberated, an unstable compound which is a good oxidizer. With hydrochloric acid in concentrated solution chromic acid interacts, producing chlorine and, by the consequent reduction of the chromic acid, chromic chloride. Thus, even in dilute solution, there is a tendency for this reaction to go on, which explains the poor keeping qualities of the mixed solution. The action of the intensifying solution upon the plate may, therefore, be considered to consist first in an oxidation of silver to silver oxide. This, in presence of hydrochloric and chromic acids, will be, at least superficially, converted to silver chloride and silver chromate, since both are insoluble substances. But in the oxidation of the silver an equivalent amount of chromic acid is reduced, possibly forming an approximation to chromic oxide because of the presence of an abundance of water and the small concentration of the hydrochloric acid. The exposure to light reduces the silver salts to subsalts, after which the reducing agent of the developer causes the redeposition of elementary silver. But along with this action there has been formed a corresponding quantity of chromic oxide, more or less hydrated, and quite insoluble, the addition of which to the original silver causes a considerable increase in the opacity of the negative.

Occasionally, even the most expert photographer will find himself possessed of a negative which is altogether too dense throughout. The matter may be remedied by submitting the plate to the process which, photographically, is known as "reduction," but which consists, chemically, simply in the oxidation of some of the silver of the image and the conversion of the oxidized silver to a soluble compound, which is then removed in solution. There is a considerable number of oxidizing agents which can be utilized for this purpose. It has been found possible so to regulate the action of some of these as to produce somewhat different results with the different oxidizers. In the case just mentioned, where there is a general opacity all over the plate, it may be desirable to diminish this opaqueness with a fair degree of uniformity throughout the scale of gradation.

If so, the "permanganate reducer" may be employed, since it gives a nearly uniform reduction, acting only a little more strongly upon the highlights (*i.e.* the densest deposits of silver) than upon the shadow details. To prepare the solution, dissolve 0.5 gram of potassium permanganate in 200 cubic centimeters of water and add 2 cubic centimeters of concentrated sulphuric acid. This stock solution is four times too concentrated, so that in using it for the reduction of a plate one part of the permanganate is to be diluted with three parts of water. The negative, if dry, is well soaked and then immersed in the solution until sufficiently reduced in density. The dish must be constantly rocked to secure uniformity of action. The plate is next quickly rinsed in two or three changes of water and transferred for five minutes to a previously unused acid thiosulphate fixing bath, and finally washed and dried. Reaction:

Silver + Potassium permanganate + Sulphuric acid
= Silver sulphate + Potassium sulphate
+ Manganese sulphate + Water

The products of this reaction are all soluble in water and therefore removable from the gelatine by washing. The function of the thiosulphate bath is to stop instantly the action of the small amount of acidified permanganate which is retained by the gelatine after the plate has been rinsed, since it would continue to dissolve away a little more silver. Reaction:

Sodium thiosulphate + Potassium permanganate
+ Sulphuric acid
= Sodium sulphate + Potassium sulphate
+ Manganese sulphate + Water

A reduction method which is very useful for over-exposed, or foggy, or veiled, negatives is the one which for a long time has been known as "Farmer's reducer." The solution consists of a mixture of ten per cent. potassium ferricyanide with ten per cent. "hypo," and acts more energetically upon the details in the shadows than upon the highlights. The result is therefore an increase of contrast, desirable for the class of negatives noted. This reducing bath, which must be made up just before it is needed, can be conveniently prepared by dissolving 10 grams of sodium thiosulphate in water and diluting to 100 cubic centimeters, and lastly adding 5 to 10 cubic centimeters of a ten per cent. ferricyanide solution. Evenness of action is secured, as usual, by rocking the tray in which the operation is conducted. Wash the plate well afterwards. Reaction:

Silver + Potassium ferricyanide + Sodium thiosulphate
= Silver-sodium thiosulphate + Potassium-sodium ferrocyanide

Two excellent processes, whereby the contrast of a plate may be diminished, are found in the ceric sulphate and the ammonium persulphate reducers, the latter being known as "Bennett's reducer." In the former, advantage is taken of the powerful oxidizing action of the cerium compounds in which cerium is in the higher condition of oxidation, having present also an acid, such as sulphuric acid, with which the oxidized silver forms a soluble product. A stock bath may be made up by dissolving 10 grams of ceric sulphate crystals in water, acidifying with 4 cubic centimeters of concentrated sulphuric acid, and diluting this mixture with water to 100 cubic centimeters. Take for use one part of the stock solution and one part of water. It will be found to attack the highlights more strongly than the details in the shadows. After reduction, wash well and dry the plate. Reaction:

Silver + Ceric sulphate + Sulphuric acid
= Silver sulphate + Cerous sulphate + Water

For "Bennett's reducer" make the following solution: Dissolve in water 12 grams of ammonium persulphate, add 2 grams of sodium sulphite and 1 cubic centimeter of concentrated sulphuric acid, and dilute to 100 cubic centimeters. Use this solution in the proportion of one part to four to eight parts of water, and apply it to the wet negative, rocking the tray while the action is going on. Rinse the plate quickly and immerse it for six minutes in a ten per cent. acid "hypo" fixing bath, which will stop the action in the same way as with the permanganate reducer. In order to get the full advantage of this method in lessening the contrasts of a negative, it is important not to allow the persulphate to act too long upon the plate. For a limited time the solution will dissolve away the densest portions of the deposited silver without appreciably attacking either the middle tones or the finest details in the shadows. But if the plate is left for a longer time in the bath, the shadow details will be materially affected. Therefore, it is necessary to watch the operation closely, removing the negative from the persulphate solution the instant that a solvent effect appears in the thinner parts. Reaction:

Silver + Ammonium persulphate
= Silver sulphate + Ammonium sulphate

It is, perhaps, more frequently the case that both these kinds of processes, of intensification and reduction, will be utilized, than that either one of them will be applied alone. For example, when the range of contrast of a given subject that must be photographed is too great to be expressed by the emulsion, it is quite feasible to adjust the exposure and the development to the shadow details, and, after fixing and washing the plate, first reduce the highlights with persulphate and then, if required, intensify the whole negative, as with the uranium bath. By this means a pleasing picture can oftentimes be made, under unfavorable conditions of lighting, showing the subject which is photographed as it appears when advantageously lighted. These purely chemical methods of modifying the negative will be found among the most useful helps to the photographer in saving numbers of negatives which would otherwise be wasted.

CHAPTER VIII

Printing Processes with Silver Salts

THE object of all the solicitude which has been expended in exposing the plate, in carrying out its development, and in any subsequent treatment applied to it is merely to provide a means for expressing in the final print the varied tones of light and shade which, photographically speaking, constitute the subject portrayed. Whether it be the photographer's purpose to make a picture which shall record facts as accurately as possible or whether it be his intention to represent a mood or a phase of the subject, giving expression in the print to his own artistic feeling, the quality of the negative determines very largely the quality of the finished picture. Successful photography depends in the first instance upon the worker's ability to make properly exposed and developed negatives. But in the wide range of printing media at his command, and especially in view of the variety of qualities and surfaces in which the popular brands of papers may be obtained, there is the possibility of a considerable degree of control. It becomes, therefore, a matter of no small importance to select a medium which is suitable for the purpose in hand, whatever it may be, and to determine the precise character of negative best adapted for printing in that medium. All printing processes depend, for their effect, upon the use of a substratum or support, which is, nearly universally, white paper, or paper that is at most but slightly tinted. The highest light is thus the plain, unshaded paper, the deepest shadow is formed by deposits heavy enough to obscure the paper entirely, and the intermediate tones are produced by the different densities of deposit, which, veiling the substratum to different degrees, allow the transmission of more or less light by the deposit and its reflection by the substratum. Since not only are most of the printing processes which depend upon silver salts the simplest to use, but also, largely for that reason, of course, are they undoubtedly the most extensively employed, we shall begin with them our discussion of the different methods of making prints.

The action of light upon silver compounds, and in particular its effect upon the silver halogen salts, whereby, according to the reaction:

Silver chloride + Light
= Silver sub-chloride + Chlorine,

the so-called latent image is formed, has already been sufficiently described in previous chapters. But in the case of photographic papers, as compared with plates or films, we must note that there are certain differences produced by the use of the different kinds of support. In the plates and films we find a comparatively thick layer of photographic emulsion spread upon glass and celluloid, respectively, both these substrata possessing no appreciable chemical activity towards the emulsion. Paper, however, is an organic substance, which, consisting largely of cellulose, is readily capable of interacting chemically, especially with silver compounds. It is, moreover, necessary, in order that the deposited silver should be kept strictly upon the surface, that the paper support be thoroughly sized. And this sizing, generally arrowroot, starch, or gelatine, is also organic and chemically active in the same way as the paper. In the sunlight printing paper, P.O.P., as it is called, there is the further difference that the light is allowed to produce a visible effect, whereupon, instead of its being treated with a reducing agent, the image is acted upon by metallic salts. By these, in conjunction with the fixing bath, a part of the silver salt is removed and the final image consists of silver and some other metal or metallic compound added to it. For making this printing-out paper there is required a binding material in which the photo-sensitive silver salt may be formed. Albumen, collodion, and gelatine are three such binders which have been much used, the last probably being most employed at the present time. A salt bath is prepared containing soluble chloride and the binder, and the sheets of paper are given a coating, which can very simply be done by floating the paper upon the solution. After it has been dried, the "plain salted paper" is again floated, upon a silver nitrate solution of suitable concentration, and dried in non-actinic light. It is then ready for use, but thus prepared has the disadvantage of not keeping well for any considerable length of time. For the salt bath, make up a solution consisting of:

Ammonium chloride.........	6 to 8 grams
Sodium citrate..............	10 grams
Sodium chloride.............	2 to 3 grams
Gelatine....................	1 gram
Distilled water, to..........	440 cubic centimeters

First, dissolve the gelatine in hot water and then add the other compounds and filter the resulting solution. Pour the solution into a tray of sufficient size. Grasp a sheet of the paper to be salted by two diagonally opposite corners and bend the sheet upon the other diagonal as an axis, by bringing the hands together. Lower the paper until it touches the surface of the liquid along the axis, and then by separating and lowering the hands allow the full area of the sheet to lie, without any air bubbles, upon the solution. Float the paper thus for three minutes, after which it is to be removed slowly and hung up by one corner to dry. It is then ready to be sensitized by similar flotation upon a solution of silver nitrate in the proportion of one part of the solid to nine parts of water. In hot weather the salted paper may be floated for three minutes, but in cold, for five minutes. Again hang up the sheet by one corner to dry, but as it is now light-sensitive, drying must take place away from actinic light. The keeping qualities of this paper, as previously stated, are poor, as it will be good for about two days in warm, but for a week in cold, weather. The paper, however, can be "salted" in quantity and sensitized only as desired.

It is now in order to consider the changes which occur in the printing, toning, and fixing of such paper. First it will be apparent that there is present in the very thin coating of the unprinted paper a considerable number of substances, since, from the nature of the operations just described, it is impossible for all of even the soluble products of the reactions to escape. When the salted paper is sensitized upon the silver nitrate, the following reactions must occur:

(1) Ammonium chloride + Silver nitrate
= Silver chloride + Ammonium nitrate
(2) Sodium chloride + Silver nitrate
= Silver chloride + Sodium nitrate
(3) Sodium citrate + Silver nitrate
= Silver citrate + Sodium nitrate
(4) Organic compounds in sizing and paper + Silver nitrate
= Complex organo-silver compound + Nitric acid

All of these insoluble silver compounds and greater or less amounts of the soluble products of the reactions, besides a portion of the silver nitrate from the sensitizing bath, will be present in the coating and soaked up in the body of the paper support. The silver-organic compound is an exceedingly complex substance whose nature is not at all well understood. It is said to be somewhat less easily formed, that is, is rather more soluble, than silver chloride, and therefore the sensitized paper will in general have more of the chloride than of the organic compound formed upon it, the relative proportions of the two depending directly upon the concentrations of silver nitrate in the sensitizing bath and chloride in the salted paper. If the sensitizing solution is, for example, sufficiently dilute, practically none of the organic silver compound will form, since all the silver from the solution in contact with the paper will go to form chloride. This organic compound is, before exposure to light, decomposed by sodium thiosulphate, and by the action of light is reduced to an organic silver oxide possessing a reddish tint. When the photochemical reaction:

Silver chloride + Light
= Silver sub-chloride + Chlorine

takes place on exposure of the paper to light, the liberated chlorine, by a secondary reaction, forms with the excess of silver nitrate present more silver chloride:

Silver nitrate + Chlorine + Organic matter
= Silver chloride + Nitrated organic matter

This new silver chloride is also photo-sensitive, and thus the quantity of sub-chloride is increased. If the printed paper is at once put into sodium thiosulphate solution to remove unreduced silver salt, as must ultimately be done to get a permanent print, the silver chloride remaining is rendered soluble as silver-sodium thiosulphate, and the silver sub-chloride is so acted upon as to form this same soluble compound and elementary silver. The reddish reduction product from the complex silver-organic substance is practically unaffected by thiosulphate. Reactions:

(1) Silver chloride + Sodium thiosulphate
= Silver-sodium thiosulphate + Sodium chloride
(2) Silver sub-chloride + Sodium thiosulphate
= Silver + Silver-sodium thiosulphate + Sodium chloride

So the image left after fixing and washing, of a rather unpleasant red color, consists of metallic silver and complex silver-organic compounds. Papers sized with gelatine give redder tones than albumen papers, and those sized with starch, bluer tones. If the prints on these papers are merely fixed after being exposed to the action of light, therefore, the resulting pictures, being very unattractive, are totally unsatisfactory, except for use as proofs. By treating them, before fixing in thiosulphate, with a suitable solution of gold chloride, the resultant color of the mixture of silver and gold may be made very pleasing. If a gold tri-chloride solution be used upon paper from which the excess of silver nitrate has been washed before toning, the reduction of gold is accompanied by a simultaneous oxidation of the sub-chloride of silver, and the latter compound is finally removed as soluble thiosulphate. In this way one atom of gold will replace three atoms of silver, and the outcome of the reaction will be a feeble blue deposit of gold, as

3 Silver sub-chloride + Gold trichloride
= Gold + 3 Silver chloride

But if the gold solution is so regulated that the trichloride is reduced to monochloride, that is, auric chloride is converted by reduction to aurous chloride, then, in the reaction between the aurous chloride of the toning bath and the silver sub-chloride of the print, there will be a replacement, atom for atom, of gold for silver, and a stronger image will result. Reaction:

Silver sub-chloride + Aurous chloride
= Gold + Silver chloride

In making up gold toning solutions auric chloride is the form of gold compound used, but it is necessary either to use hot water for dissolving the salts, and then wait for the solutions to become cool, or to allow the cold solutions to stand for a day or two before using them. In this manner the auric salt is partially reduced to aurous chloride in the solution, after which action the toning baths work properly. Such a toning bath is the following recommended by Abney:

Gold trichloride........................	1 part
Calcium hypochlorite ("Chloride of lime")	1 part
Calcium carbonate ("Chalk")...........	1 teaspoonful
Water..................................	3500 parts

If this bath is made up with hot water it can be used as soon as it has cooled. Gold trichloride as usually prepared contains an excess of free hydrochloric acid, and it is partly for the purpose of neutralizing the acid that the calcium carbonate is added to the bath. Reaction:

Calcium carbonate + Hydrochloric acid
= Calcium chloride + Carbon dioxide + Water

Some salts have the property of interacting to a greater or less extent with water in which they are dissolved, the reaction being called "hydrolysis." It is practically the reverse of a reaction of neutralization in which base and acid unite to form a salt and water, since in hydrolytic action a salt and water interact to form a base and an acid. Calcium hypochlorite hydrolyzes in this manner to some degree, and hypochlorous acid and calcium hydroxide tend to form in the solution. Likewise, when auric chloride is contained in the same solution with the calcium hydroxide, it may be considered to react with the latter to produce aurous chloride, calcium hypochlorite, and water, thus:

Auric chloride + Calcium hydroxide
= Aurous chloride + Calcium hypochlorite
+ Water

A similar reaction may occur with the solid calcium carbonate placed in the toning bath:

Auric chloride + Calcium carbonate
= Aurous chloride + Calcium hypochlorite
+ Carbon dioxide

The gold salt in such a solution may be said to be chemically in a state of neutral equilibrium; the least disturbance renders the equilibrium unstable, and metallic gold begins to precipitate. If into this bath there is put a print, owing to the presence of the subchloride of silver and the light-reduced, silver-organic oxide, the chemical balance of the solution is upset, gold commences to separate, and the sub-compounds of silver are, by chlorine from the aurous chloride, oxidized back to silver chloride, according to the reaction previously written. Before toning with the gold solution it is usual to wash the printed paper in several changes of water in order to free it as much as possible from silver nitrate. Any soluble silver salt not washed out of the paper is at once precipitated in the toning bath as silver chloride by action of the gold chloride. The hypochlorite acts as a restrainer in the bath, retarding the reduction of gold. Perhaps it does this in two ways, since not only does hypochlorous acid decompose spontaneously, forming hydrochloric acid and oxygen, by the reaction:

Hypochlorous acid = Hydrochloric acid + Oxygen

but it also reacts with hydrochloric acid directly, liberating chlorine:

Hypochlorous acid + Hydrochloric acid
= Chlorine + Water

The oxygen evolved must tend to reoxidize the gold, thus diminishing its rate of reduction; and the free chlorine also tends to retard this reduction by oxidizing the sub-chloride of silver directly. Evidently, from these considerations, the bath should be expected to become acid in time, and this is in fact the case.

Another toning solution may be prepared from sodium acetate and gold trichloride, but it must be made up the day before it is to be used, to allow the partial reduction of auric to aurous chloride to occur. Afterwards it keeps indefinitely, and, like the preceding bath, it may be strengthened by the addition of more gold trichloride as it becomes worked out.

Sodium acetate........................	30 parts
Gold trichloride.......................	1 part
Water.................................	4,400 parts

This formula also is given by Abney. Aurous chloride may be formed by the following reaction, in the ripening of the bath:

Auric chloride + Sodium acetate
= Aurous chloride + Sodium trichloracetate
+ Hydrochloric acid

In using the solution the print must first be well washed to free it from the greater portion of silver nitrate. This bath also becomes after a time too acid to work well. The reaction, by which metallic gold is substituted for silver, is the same as previously given:

Silver sub-chloride + Aurous chloride
= Gold + Silver chloride

The unfixed image, therefore, after toning, is composed of metallic gold and the chloride of silver, together with any sub-chloride of the latter metal which has not suffered oxidation.

To fix prints after toning, they should be well washed in water and then put for ten to fifteen minutes into a plain solution of sodium thiosulphate, one part, to water, five parts; after this they may be soaked for fifteen minutes and finally washed in running water for twelve hours. Reaction:

Silver chloride + Silver sub-chloride
+ Sodium thiosulphate
= Silver + Silver-sodium thiosulphate
+ Sodium chloride

The tones of the print are, in part, caused by the various sizes of the particles of gold deposited, the color by reflected light of finely divided gold ranging from purple to a dirty green, according to the fineness of the subdivision. An over-toned print is blue on account of the excess of gold deposited. The final tone of the fixed print is due to the mixture of colors, by reflected light, of the silver and gold of which the image is composed. Before fixing, the print can be further washed and put into a solution of a platinum salt in which the gold will be partially replaced by platinum, in a similar way as the gold itself was plated upon the silver.

Formulas for the platinum toning of printing out paper are the following:

Potassium chloroplatinite..	2 grams
Phosphoric acid (Sp.G. 1.12)	28 cubic centimeters
Water (distilled), to.......	1000 cubic centimeters

After toning, the print is to be washed and then fixed in thiosulphate and washed as usual. Or:

Potassium chloroplatinite..	0.25 gram
Sodium chloride..........	2.5 grams
Citric acid...............	2.5 grams
Water (distilled), to.......	500 cubic centimeters

To use this solution, tone first in an ammonium sulphocyanide bath, wash, and put into the platinum bath, and finish as usual. The sulphocyanide bath will be given presently.

A gelatine emulsion, originated by Abney, which can be coated upon paper for prints or upon glass for transparencies, is prepared in much the same way as the gelatino-bromide emulsion for plates:

1.	Sodium chloride..........	3.7 grams
	Potassium citrate.........	1.8 grams
	Water, to................	50 cubic centimeters
2.	Silver nitrate.............	11 grams
	Water, to................	50 cubic centimeters
3.	Gelatine.................	15 grams
	Water, to................	175 cubic centimeters

After 2 and 3 have been mixed, 1 is to be added in small quantities successively with shaking. When the emulsion has set, squeeze it through cloth into cold water, and allow it to soak for ten or fifteen minutes. Pour off the water, drain the emulsion, and dissolve it, with the aid of heat, with 15 cubic centimeters of alcohol. Paper is best coated with this mixture by flotation. After printing, the paper can be either fixed at once, which will give a brown color, or it can be toned in a bath made up of ammonium sulphocyanide and gold trichloride:

Ammonium sulphocyanide...	7 grams
Gold trichloride............	0.12 gram
Water, to..................	1000 cubic centimeters

The gold salt and ammonium sulphocyanide interact to form a soluble double compound, according to the equation:

Gold trichloride + Ammonium sulphocyanide
= Ammonium-gold sulphocyanide
+ Ammonium chloride

Gold is reduced from the double salt by the action of silver sub-chloride, perhaps as follows:

Silver sub-chloride + Ammonium-gold sulphocyanide
= Gold + Silver chloride + Ammonium
sulphocyanide + Silver sulphocyanide

The toned print is rinsed, fixed in thiosulphate solution, and washed. Chloride printing out papers are manufactured in which the toning salts are incorporated in the emulsion, so that after printing it is only required to immerse the dry print in a thiosulphate bath, in which the toning proceeds simultaneously with the fixing. These are the "self-toning" papers. But it is at least sometimes true that the attempt to secure too great simplicity in photographic manipulations may lead to results less permanent and inferior in beauty.

The foregoing criticism does not necessarily apply to the second great order of silver papers, namely, the developing out papers. For certainly, if they are worked with sufficient care, there appears to be no reason why they should not be as permanent as a print in silver can be made, or, allowing for the difference between the paper and glass supports, why they may not be practically as permanent as the negative itself. The chief cause of the lack of permanency in silver images seems to be the incomplete removal of thiosulphate, which in the course of time breaks down, being in reality a none too stable substance, and liberates sulphur. This produces a yellowing of the paper. Besides this, if any intensification or toning processes are applied to an image which still retains thiosulphate, there will inevitably occur in time complicated reactions by the products of which the plate or print will be stained or bleached. In the making of photographs, by whatever method, there is no "dodge" nor "trick" which can possibly surpass an intelligent grasp of the chemical principles involved, if coupled with a strict application of good laboratory practice.

The developing papers are subdivided into two classes, those in which silver chloride is the sensitive salt and those in which silver bromide is used. In the former, or "gaslight" papers, the light sensitiveness is not too great to permit of handling the paper in the weaker illumination of an ordinary room lighted by lamps, so that the darkroom is eliminated. But in the case of the bromide paper the sensitiveness, approximately one twentieth of that of the photographic plate, is so great that the paper must be carefully protected from white light. The action of light upon these salts, in the formation of the latent image, and the development of the image have already been discussed in their respective chapters, and nothing further need be added here upon these points. The principal precautions to be taken in working these papers are to use a developing agent which gives a good black deposit of silver, to adjust the solution so that staining is prevented, and to fix thoroughly and in a fresh "hypo" solution, finally freeing the paper as completely as possible from all removable substances by sufficient washing.

If it is desired to alter the ordinary black deposit of silver to some color, there is available a considerable number of processes for the purpose. The change most commonly made is from black to sepia, and this is effected by transforming the silver image into one composed of silver sulphide. There are two methods of doing this, as shown in the experiments.

Experiment 31. Make up 500 cubic centimeters of a solution containing 35 grams of sodium thiosulphate and 7 grams of powdered potassium alum, heating the water to boiling for the purpose. Put into this (unfiltered) bath a well-washed print and observe the alteration of the black image to brown.

In the process the thiosulphate is decomposed and the sulphur combines with the silver, forming silver sulphide. The slow breaking down of the thiosulphate is due to the fact that aluminum salts hydrolyze, tending to go over to aluminum hydroxide, thus liberating acid in the solution. This acid causes the decomposition of the thiosulphate. The action may be represented as follows by equations in steps:

1. Potassium aluminum sulphate + Water
   = Potassium aluminum hydroxy-sulphate
   + Sulphuric acid
2. Sodium thiosulphate + Sulphuric acid
   = Sodium sulphate + Sulphur + Sulphur dioxide
3. Silver + Sulphur = Silver sulphide

A better way of changing the silver to silver sulphide consists in first oxidizing the image, as to silver bromide, and then treating it with a solution of a sulphide, whereby silver sulphide is formed by metathesis.

Experiment 32. Dissolve 5 grams each of potassium ferricyanide and potassium bromide in enough water and dilute to 250 cubic centimeters. Put a dry print into this solution until completely bleached. Rinse the print thoroughly and transfer to a solution of sodium sulphide, in which the formation of silver sulphide gives the sepia color.

The stock sulphide solution is prepared by dissolving 25 grams of pure sodium sulphide in 250 cubic centimeters of water. If impure sodium sulphide is used, dissolve in 150 cubic centimeters of water, boil, and dilute to 250 cubic centimeters. The impurity is precipitated and will settle to the bottom, where it may be left, the liquid being decanted as desired. For use, take 10 cubic centimeters of the stock solution and dilute to 200. Leave the print in this diluted solution until it is certain that the action is complete, wash it in running water for about 15 minutes, and dry it. The reactions which take place may be represented as follows:

1. Silver + Potassium ferricyanide + Potassium bromide
= Silver bromide + Potassium ferrocyanide
2. Silver bromide + Sodium sulphide
= Silver sulphide + Sodium bromide

Another process of sulphide toning, by which it is possible to control the depth of the tone, is one in which mercuric chloride is added to the bleaching solution. By varying the proportions of the mercury salt, a range of browns from sepia to a pure black can be secured. This process is naturally not quite so simple as the preceding. Two stock solutions which keep well are required for bleaching:

1.	Potassium ferricyanide....	30 grams
	Potassium bromide.......	45 grams
	Water, to................	250 cubic centimeters
2.	Mercuric chloride.........	7 grams
	Potassium bromide.......	7 grams
	Water, to................	250 cubic centimeters

The prints to be toned should each have been fully developed in fresh developer, and dried after fixing and washing, before toning. For sepia, take 1 part of No. 1 and dilute with 11 parts of water. One part of No. 1, 1 of No. 2, and 10 of water give a colder brown, and as the relative proportion of the second solution is increased, the tone approaches nearer to black. For deep brown, take ¾ part of No. 1, 1 part of No. 2, and 10¼ parts of water; brown-black, 1 of No. 1, 2 of No. 2, and 13 of water; and for a pure black, ½ of No. 1, 2 of No. 2, and 9½ parts of water. In every case the bleaching should be thorough, and if any of No. 2 solution is used in the bath the bleached prints after being well washed must be transferred for two or three minutes to a dilute solution of hydrochloric acid, 3 cubic centimeters of the concentrated acid in 200 cubic centimeters of water, in order to prevent the mercury salts from combining with the gelatine coating. Move the prints on into a second and third similar acid bath, and finally wash for twenty minutes. After this the sulphide toning is carried out in a bath made by diluting to 200 cubic centimeters 15 cubic centimeters of the stock solution of sodium sulphide above described. The diluted sulphide toning solution should be used but once. After toning, the print is to be thoroughly washed, say for a half hour, and then dried. Printing-out paper cannot be successfully sulphide-toned. The reactions may be outlined thus:

1. Silver + Potassium ferricyanide
+ Potassium bromide
= Silver bromide + Potassium ferrocyanide
2. Silver + Mercuric chloride
= Silver chloride + Mercurous chloride
3. Silver bromide + Sodium sulphide
= Silver sulphide + Sodium bromide
4. Silver chloride + Sodium sulphide
= Silver sulphide + Sodium chloride
5. Mercurous chloride + Sodium sulphide
= Mercuric sulphide + Mercury + Sodium chloride

The toned image is therefore composed of silver and mercuric sulphides with elementary mercury, if any of the No. 2 bleaching solution is included in the bath. The character of the tone is determined by the proportion of black mercury and black mercuric sulphide added to the brown silver sulphide image.

For producing a variety of colors, some ranging from a warm black through brown to red, and for blues and greens, salts of copper, uranium, iron, and vanadium are used. So far as concerns the permanency of the results, it is well to observe at the start that the pure silver image and the image in silver sulphide may be considered sufficiently durable if the chemical work is well done. But when the simple metallic silver image is converted into complexes containing silver salts with copper, uranium, iron, or vanadium compounds respectively, the way is opened not only for the gradual decomposition of these complicated bodies, but more especially for the attack upon them of an atmosphere containing moisture and other impurities. Consequently the experimenter should, knowing the dangers, pay all the more attention to cleanliness in manipulation and in particular to the thoroughness with which soluble products are washed out of the prints; and even then should not be unprepared for alterations in them in the lapse of time.

It will be most convenient to make up a number of stock solutions from which the different toning baths can be quickly and easily prepared whenever wanted:

SOLUTION A

Potassium citrate............	100 grams
Water, to..................	1000 cubic centimeters

SOLUTION B

Potassium ferricyanide.......	25 grams
Water, to..................	250 cubic centimeters

SOLUTION C

Copper sulphate............	25 grams
Water, to..................	250 cubic centimeters

SOLUTION D

Uranium nitrate............	5 grams
Water, to..................	50 cubic centimeters

SOLUTION E

Ferric ammonium citrate.....	12.5 grams
Water, to..................	250 cubic centimeters

Toning with copper gives a range of colors from a warm black through brown, purple, many shades of red, to the so-called "red chalk." The image which is finally obtained consists of a mixture of silver ferrocyanide, copper ferrocyanide, and silver. Take of the solutions:

Solution A.................	100 cubic centimeters
Solution B.................	10 cubic centimeters
Solution C.................	10 cubic centimeters

and place the wet print in the mixture until it has altered to the desired color. The action may be stopped at any point by washing for ten minutes, after which the print is to be dried. The following reactions may be supposed:

1. Silver + Potassium ferricyanide
   = Silver ferrocyanide + Potassium ferrocyanide
2. Copper sulphate + Potassium ferrocyanide
   = Copper ferrocyanide + Potassium sulphate

To get red tones more quickly, an alkaline bath may be made by dissolving 2 grams of copper sulphate and 5 grams of potassium ferricyanide in 1,000 cubic centimeters of saturated ammonium carbonate solution.

By referring to the preceding chapter, it will be recalled that uranium salt is used in a process for intensifying the silver image. For this reason the uranium toning solution is not adapted to dense prints, since they are intensified by it. And, further, we remember that prolonged washing of the uranium-intensified image results in weakening it. This action is, of course, more pronounced in the case of a print, and therefore the final washing cannot be too long continued if the print is to hold its tone. This not only indicates a quite appreciable solubility of the uranium ferrocyanide, but also does not tend towards permanency of the image. Take of the stock solutions as follows:

Solution B	10 cubic centimeters
Solution D	5 cubic centimeters
Glacial acetic acid	10 cubic centimeters
Water	400 cubic centimeters

and, after the tone wished for is reached, wash the print in two or three changes of water acidified with acetic acid (one part acid to 100 parts of water), and wash not longer than 15 minutes. The colors given by this formula run from black through brown to a red that has more yellow in it than the reds given by the copper bath. The reactions are the same here as those written for uranium intensification, and therefore need not be repeated. If not enough acetic acid is used, permanent yellow stains will appear.

In order to color the print blue, take:

Water	300 cubic centimeters
Solution B	30 cubic centimeters
Solution E	30 cubic centimeters
Nitric acid (concentrated)	2 cubic centimeters

In the acidified solution the oxidation of metallic silver is accompanied by the reduction of an equivalent amount of ferricyanide to ferrocyanide, when not only is silver ferrocyanide formed, but there is produced, also, by interaction of the ferric salt present with the ferrocyanide, ferric ferrocyanide, which, as we saw in making the tests for ferric and ferrous iron, is the substance known as "Prussian blue." It is quite insoluble, and therefore adds itself to the image. Too long washing after the print has been toned tends to bleach it out, since the blue ferric ferrocyanide is after all slightly soluble in water. Reactions:

1. Silver + Potassium ferricyanide
   = Silver ferrocyanide + Potassium ferrocyanide
2. Ferric ammonium citrate + Potassium ferrocyanide
   = Ferric ferrocyanide + Potassium citrate
   + Ammonium citrate

Green tones, which become lighter with longer action of the bath, can be secured by a mixture of iron and vanadium chlorides. The solution is a rather complicated one:

NO. 1

Ferric chloride	23 grams
Oxalic acid, saturated solution	125 cubic centimeters
Vanadium chloride	4.6 grams
Nitric acid (concentrated)	10 cubic centimeters
Water, to	500 cubic centimeters

NO. 2

Potassium ferricyanide	23 grams
Water, to	500 cubic centimeters

Add No. 2 to No. 1 with constant stirring and use the mixture without further dilution. Prints should tone in 1 to 2 minutes, and are then to be fixed in a solution of:

Sodium thiosulphate..........	60 grams
Boric acid....................	12 grams
Water, to....................	300 cubic centimeters

After fixing, wash for 10 minutes. The reduction of the vanadium salt may be accomplished by both the finely divided silver of the image and the ferrocyanide produced in the reduction of potassium ferricyanide. Thus vanadium compounds in which the vanadium is present in several lower stages of oxidation are probably added to the image. Mixtures of such vanadium compounds are green. If the reduction of vanadium proceeds too far, as by allowing the print to remain in the bath too long, the resulting color is lighter owing to changes in the proportions of the coloring constituents.

Bromide paper may also be toned with a platinum solution, in which toning for about 20 minutes gives a good black:

Hydrochloric acid (concentrated)	1 cubic centimeter
Potassium chloroplatinite.......	1 gram
Water (distilled), to............	1000 cubic centimeters

The prints are washed thoroughly after toning, to get rid of the acid, are fixed in sodium thiosulphate to remove the silver chloride formed, and given a final washing. Reactions:

1. Silver + Potassium chloroplatinite
   = Platinum + Silver chloride + Potassium chloride
2. Silver chloride + Sodium thiosulphate
   = Silver-sodium thiosulphate

A similar formula may be used for toning lantern slides:

Hydrochloric acid (concentrated)	0.2 cubic centimeter
Chloroplatinic acid, 5% solution	4 cubic centimeters
Water (distilled), to	1000 cubic centimeters

This bath gives rapid toning with some reduction in density. The reactions are similar to those just given.

A great deal of study has been put by the manufacturers of photographic materials into the preparation of ready-to-use powders and solutions for performing practically all of the different chemical operations involved in the making of photographs. Doubtless these same manufacturers have spent considerable sums of money in advertising their preparations. While it is quite true that these may be on occasion extremely convenient to use, nevertheless it is equally true that it is both more costly in actual cash outlay and much less enlightening to the earnest amateur worker to make use of them. It would be idle to argue that the photographer should now, as he was once obliged to do, make his own plates, when they can be so much better and more uniformly turned out by the factories. Something can be said on both sides when it comes to the preparation of papers, for, as we shall see presently, there are several interesting and beautiful processes for homemade prints. But not only can the amateur save a little money by purchasing the necessary chemicals in bulk and making up his own solutions, he can, if he will allow himself to become interested, derive a great deal of pleasure and satisfaction from the study of the wonderful chemical processes which go to make up this fascinating art of photography, benefits that are largely lost to those who work only with ready-made materials, and entirely so to the kind that "pushes the button" and lets the professional "do the rest."

CHAPTER IX

PRINTING PROCESSES WITH IRON SALTS

IN an earlier chapter reference was made to the two classes of iron salts, ferric and ferrous, and several experiments were described in illustration of the readiness with which they can be reduced and oxidized respectively. The light-sensitiveness of ferric compounds was investigated by Sir John Herschel, and he indeed invented, in 1840, one of the simplest photographic printing processes, using salts of iron, namely, the "blue print" process.

Experiment 33. Coat a piece of sized paper with a little ten per cent. solution of ferric ammonium citrate, either by floating the paper upon the liquid or by applying the solution with a brush or a wad of absorbent cotton. When the coated paper has become dry, expose it for one or two minutes to sunlight under a negative. Develop the print in a little dilute potassium ferricyanide solution and wash it thoroughly. Note that the shadows are blue and the highest lights white. Coat another piece of paper with the same ferric ammonium citrate solution, expose it similarly under a positive transparency, such as an unmounted lantern slide, and develop with dilute potassium ferrocyanide and wash. Observe in this case also that a blue positive has been obtained, but from a positive instead of from a negative.

By the action of light the ferric citrate, in contact with the organic matter of the sizing, has been reduced to ferrous citrate. This same reaction of course takes place in both parts of the experiment. Since ferrous salts interact with ferricyanide to form an insoluble blue compound, "Turnbull's blue," the application of potassium ferricyanide to the first print, from the negative, forms blue ferrous ferricyanide wherever any ferric salt has been reduced, viz., in the shadows and half tones. The interaction of ferric salts with ferricyanide produces ferric ferricyanide, but this is a soluble compound, and therefore washing the paper sufficiently removes all the unreduced ferric salt and whatever ferricyanide is not combined in the insoluble dark blue deposit. Thus a blue and white positive is obtained by printing under a negative. Reactions:

1. Ferric ammonium citrate + Light + Organic matter
   = Ferrous ammonium citrate + Organic
   oxidation products

2. Ferrous ammonium citrate + Potassium ferricyanide
   = Ferrous ferricyanide + Ammonium citrate
   + Potassium citrate

In the second print, from the positive, the unreduced ferric compound by interaction with potassium ferrocyanide forms ferric ferrocyanide, an insoluble precipitate of dark blue "Prussian blue," in the shadows. In the highlights where the reduction of the iron salt has occurred, ferrous citrate reacts with the ferrocyanide and an insoluble precipitate results, which is originally ferrous potassium ferrocyanide and, like most ferrous salts, white. But it instantly begins to oxidize, absorbing oxygen from the air, and rapidly turns blue on account of the oxidation to ferric ferrocyanide. Thus the highlights are unavoidably stained a light blue by the mixture of white ferrous potassium ferrocyanide with dark blue ferric ferrocyanide. Reactions:

3. Ferric ammonium citrate + Potassium ferrocyanide
= Ferric ferrocyanide + Ammonium citrate
+ Potassium citrate
4. Ferrous ammonium citrate + Potassium ferrocyanide
= Ferrous potassium ferrocyanide + Ammonium
citrate + Potassium citrate
5. Ferrous potassium ferrocyanide + Oxygen + Water
= Ferric ferrocyanide + Potassium ferrocyanide
+ Potassium hydroxide

Blue print paper as commonly prepared is coated with a mixture of ferric ammonium citrate and potassium ferricyanide and dried in the dark. It does not keep well, but this disadvantage is somewhat counterbalanced by the fact that it is so easily made. When it has been fully exposed to the action of light, as under a negative or other design, it requires but a quarter of an hour's washing and subsequent drying to be completed. As soon as the printed paper is put into water, the reduced ferrous salt and the potassium ferricyanide begin to go into solution and instantly react, giving the insoluble blue ferrous ferricyanide wherever the light has acted. At the same time all the other substances dissolve and are washed away, and the print is therefore developed and fixed by the one operation. The reactions are the same as in (1) and (2) above. Washing must not be too long continued, since the blue precipitate has an appreciable solubility and the prolonged application of water degrades the image. Water containing lime (*i.e.*, hard water) has a greater solvent effect than soft water. The prints can be made somewhat brighter if citric acid be added to the first wash water, about 2 grams to each liter. If it is desired to use others than the strictly photographic papers, they should be sized. This may be done by mixing 15 grams of arrowroot to a paste with a little cold water, making it up to 600 cubic centimeters with water and boiling the mixture gently until it becomes clear. The thinner papers may be immersed in sizing them, but for thick ones it is better to brush the size on as uniformly as possible, brushing the paper one way and then across, and finally to smooth out streaks and any unevenness with a soft sponge or tuft of absorbent cotton. The sheet may then be hung up with clips until dry. As the sizing has a tendency to drain away from the upper edge and accumulate along the lower edge of a sheet so hung up, it is sometimes advisable to resize the paper and in drying hang it the other side up. But if it is permitted to become nearly or quite surface dry before hanging up, there will be no need of the second sizing. For coating the paper a mixture of two solutions is prepared:

NO. 1

Ferric ammonium citrate.....	160 grams
Water, to..................	1000 cubic centimeters

NO. 2

Potassium ferricyanide......	120 grams
Water, to..................	1000 cubic centimeters

Fresh, clean crystals of the ferricyanide are to be used. If the crystals are covered with a powder, they should be quickly washed in a little water before making the solution, and in this case a few grams more than the amount specified may be weighed out. These solutions are mixed and should be kept in a brown bottle in the dark. The mixture will keep better, and for a longer time, if potassium dichromate be added in the proportion of one gram per liter. When ready to make up some paper, filter as much of the solution as may be required and apply it evenly with a brush and tuft of absorbent cotton. The coated paper should be dried as quickly as possible in the dark.

A blue print process which is useful for making positive copies from positives is based upon the second part of Experiment 33. It is employed particularly for copying tracings, and these must in printing be put into the frame with the back in contact with the surface of the blue print paper. The coating is a mixture of ferric salt solution with a little gum arabic. After printing, it is developed in a mixture of ferrocyanide and ferricyanide, in which both the reduced and the unreduced iron salts form insoluble blue precipitates, but where the light acted the gum washes off, carrying away the blue pigment with it, so that the image consists of a blue deposit upon a white ground.

In the blue print processes the photographic image is formed directly from the iron salt itself. Ferrous compounds, as we remember, are excellent reducing agents, and upon this fact are based two printing methods which are indirect. That is, the image is deposited, of another substance from that reduced by the light, by a secondary reaction. In the first of these, the platinotype process, the final photographic image is formed in elementary platinum by the modification known as "platinum black." This finely divided dense black variety of the element is conveniently prepared by the action of suitable reducing agents upon acid solutions of platinum salts. When, as in the platinum print, it is deposited upon the surface of a very pure and durable paper, there may be produced not only an effect of extreme beauty, but probably the most permanent form in which a photograph can be made. Practically the only alteration which affects a properly made, pure paper upon which a platinum image has been superposed is a slight yellowing with age, due to iron salt which was imperfectly removed in the fixing process. The other constituent of the platinum print, namely, the elementary platinum, is one of the most resistant substances with which the chemist has to deal. In any of its forms, the element is only slightly affected by even high concentrations of the single acids, requiring aqua regia, a mixture of hydrochloric and nitric acids (generally in the proportions of three to one) to dissolve it. It is fusible only by use of the electric current or by the oxyhydrogen blowpipe, melting at over 1,700 degrees Centigrade, is at no temperature attacked by either water or oxygen, and, except in the presence of alkali, is not acted upon by sulphur. Under the conditions in which photographs are usually kept, platinum prints may therefore be considered to be perfectly permanent.

Not including the preparation of the coated paper, platinum printing consists of the same three distinct operations which have been described for the making of silver prints, viz., the exposure to light, development of the image, and the fixing of this image by removal of soluble materials. But, as has just been intimated, platinotype is somewhat different from the processes of the silver print, in that the platinum is not primarily the image-forming material, but is, by a supplementary reaction, substituted for the original image, which is, in fact, formed in photo-chemically reduced iron salt. When the thin film of mixed ferric and platinous salts spread upon paper is subjected to the action of light, the reduction to ferrous salt produces a very pale and unpromising appearance, the picture showing in a faint brown upon a yellow ground. Reaction:

Ferric oxalate + Light = Ferrous oxalate + Carbon dioxide

The platinum salt, during and after the exposure, itself practically unaffected, is in the presence of a ferrous compound, but the two are inactive towards each other in the dry state. Thus at this stage no elementary platinum is in the image, unless by the access of moisture from the air the substances come into chemical contact by commencing to dissolve. In order that the reducing power of ferrous iron may have full play upon the platinum salt, it is necessary to bring the iron into solution together with the platinum. This, with the water-insoluble ferrous oxalate, which is the form of ferrous salt used, can be done by treating it with a solution, which is used warm (not below 15.5 degrees Centigrade or 60 degrees Fahrenheit), of potassium oxalate, 26 grams of the salt in each 100 cubic centimeters of solution. By this means the insoluble ferrous oxalate image is altered to the soluble double ferrous potassium oxalate. This at once reacts with the dissolved potassium chloroplatinite, and platinum black is deposited by reduction in place of the iron salt. As the quantity of platinum reduced is equivalent to the amount of ferrous salt, and this last is proportional to the exposure, the varying densities of the silver deposit of the negative are inversely repeated in varying densities of platinum black upon the paper. Reactions:

1. Ferrous oxalate + Potassium oxalate
   = Ferrous-potassium oxalate
2. Ferrous-potassium oxalate
   + Potassium chloroplatinite
   = Platinum + Potassium chloride
   + Ferric-potassium oxalate

In this condition the print is saturated with a solution containing whatever unreduced potassium chloroplatinite is left, ferric-potassium oxalate, and potassium chloride. All of these, but the iron salt especially, must be washed out of the paper in order that no changes may later take place in the picture. If the print were simply washed with plain water, as the concentration of the iron compound diminished the tendency of ferric salts to hydrolyze in dilute solutions would become apparent in the formation of an insoluble basic (hydroxy-) ferric compound. Reaction:

Ferric oxalate + Water
= Ferric hydroxy-oxalate + Oxalic acid

No amount of water would serve to effect its complete elimination from the paper. For these reasons, the first wash waters into which the developed platinum prints are put must contain small quantities of hydrochloric acid, about 10 cubic centimeters of the concentrated acid to each 600 cubic centimeters of water. Since the basic ferric compounds are soluble in hydrochloric acid, presence of the acid prevents their formation. Reaction:

Ferric hydroxy-oxalate + Hydrochloric acid
= Ferric chloride + Ferric oxalate

Several of these acid iron-clearing baths must be used and the paper passed along from one to the next, draining each print as thoroughly as possible from one solution before putting it into the succeeding bath. At least four or five of these clearing-solutions should be used, prints being allowed to stay in the first one for ten minutes and in each of the others for five. The last one, while in use, must show no trace of yellow color, indicating that there is in it only an inappreciable amount of iron salt. After this, a fifteen minutes' washing in water will be ample, or half an hour if the paper is very thick. The amount of ferric salt left in the print as it comes out of the last acid clearing-bath may be indicated by catching the drainings from the paper in a test tube and adding a drop of ferrocyanide solution.

Most of the soluble platinum salt will be retained in the first washing tray, and, if much work in platinum is done, it will be worth while to save not only this first clearing-bath, but also all old developing solutions and scraps of paper. The paper is burned and the ashes saved. Solutions are best treated by pouring them all together in a jar, adding a little hydrochloric acid, if the mixture does not already contain an excess, and suspending in it, a little above the bottom, some metallic zinc. The zinc goes into solution, while the platinum separates out. Reactions, using platinic chloride as a type:

1. Platinic chloride + Zinc
   = Platinum + Zinc chloride
2. Zinc + Hydrochloric acid
   = Hydrogen + Zinc chloride
3. Platinic chloride + Hydrogen
   = Platinum + Hydrochloric acid

After sufficient standing, the solution will have become decolorized, owing to the deposition of all the platinum and the reduction to the ferrous condition of all the iron salt. When this is the case, most of the liquid can be carefully decanted, or siphoned, from the precipitate which has settled to the bottom, after which more waste liquids may be introduced into the jar and the recovery process continued. When enough solid material has accumulated, it is separated on a filter, washed with hot water, and, combined with all the solid residues on hand containing platinum, boiled in a porcelain dish with aqua regia until complete solution of the platinum is effected. Evaporate the liquid down on a water-bath adding a little hydrochloric acid before it comes to dryness, and evaporate again, to boil out the nitric acid. Repeat the evaporation to the crystallizing point with hydrochloric acid to make sure that all nitric acid is expelled; dilute up with enough water and filter the solution. Add an excess of sodium carbonate and a little alcohol and boil the mixture, which will precipitate the platinum as a black powder. Wash it with hot water and afterwards with hot hydrochloric acid and dry it thoroughly and weigh it. Dissolve in aqua regia, evaporate down with hydrochloric acid several times as before to free it from nitric acid, add one gram of potassium chloride for each gram of platinum present, and dilute with just enough distilled water to get the potassium chloroplatinate all in solution. Each gram of platinum will make about 2.5 grams of potassium chloroplatinate. The solution is next to be so adjusted that for each two grams of the chloroplatinate there will be 25 cubic centimeters of water (distilled) and one gram each of acid potassium sulphite and potassium chloride. This mixture is boiled for twenty-five minutes, counting the time from the actual commencement of ebullition, is then cooled, put in a shallow dish, such as a thoroughly cleaned tray, and left to crystallize. Red crystals of potassium chloroplatinite will separate out; they should be recrystallized several times to purify them, and when carefully dried the salt is ready for use in making up homemade platinotype papers.

The following formula, suitable for the so-called "cold bath development," is recommended by Abney, not only on account of the keeping qualities of the paper prepared with it, but also because, by variations in the developer, the prints are susceptible of considerable modification:

NO. 1

Ferric ammonium oxalate	50 grams
Water, distilled	50 cubic centimeters
Oxalic acid, 10 per cent. solution	15 cubic centimeters

NO. 2

Potassium chloroplatinite	1 part
Water, distilled	5 parts

NO. 3

Ammonium dichromate	4 grams
Water, distilled, to	100 cubic centimeters

For each sheet of paper 20 inches by 26 inches, take 8 cubic centimeters of No. 2, mix with 4 cubic centimeters of No. 1, and 8 cubic centimeters of No. 3. Unsized papers must be given a good sizing with gelatine (or arrowroot may be used):

Gelatine	1 gram
Water	100 cubic centimeters
Potassium alum	0.3 gram
Methyl alcohol	25 cubic centimeters

Swell the gelatine thoroughly in the water and afterwards dissolve it by heating, then add the powdered alum and methyl alcohol. Filter while hot through muslin, taking care to avoid bubbles. Paper may be treated with the sizing by immersion or by coating with a brush, in the manner previously described in the present chapter. In applying the sensitive coating to the paper, it must be remembered that we are dealing with a very unstable mixture. For this reason an ordinary bristle brush will not serve, as it will soon become saturated with the decomposition products of the solution, and these will be transferred to other sheets, with very disappointing results when made into prints. A form of brush, figured and described by Abney, is made out of a 3¼ inch by 4¼ inch piece of photographic film, (*i.e.* an old negative), strips of cotton flannel to fit it, and a film clip such as is used for tray development of roll films. A strip of the flannel is laid, fleece out, upon the celluloid, and the ends of both are then doubled back, without creasing the film, with the cloth on the outside, until they can be firmly held together with the clip. The clip becomes a convenient handle, and the resiliency of the celluloid gives plenty of stiffness without the rigidity which would abrade the paper. For each large sheet a fresh cloth covering must be used, but when smaller sheets of paper are coated, several may be done before renewing the flannel. In any event it is not advisable to use the same piece longer than 10 to 12 minutes. The sheet of paper to be coated may be pinned, the sized side up, at one end upon a board and grasped at the other by the fingers of the left hand. This will allow for the expansion which results from wetting it with the solution. A measured amount of the sensitizing liquid, proportioned to the dimensions of the sheet as given above, is poured upon the middle of the paper and as rapidly as possible brushed with the spreader in circular sweeps out into the corners and over the entire surface. After this the strokes are criss-crossed and all uneven places blended out as much as may be. The next part of the operation consists in the surface-drying of the coated sheet, which is allowed to occur spontaneously, but should not be achieved in under five nor over ten minutes. If dried too quickly the sensitizer will be liable to come off in the developer, but if drying is too slow it may soak into the body of the paper, which produces flat and foggy pictures. When surface-dry, the paper is completely dessicated over a stove at a temperature not too great for the hand to bear (not to exceed 40 degrees Centigrade), this change being indicated by a deepening of the color. The paper, when dry, must be kept dry, which means very dry indeed, since if any moisture is absorbed traces of the iron and platinum salts immediately go into solution. In this condition not only is the ferric oxalate more unstable and therefore liable to spontaneous decomposition, but also as soon as the sheet is exposed to light and the ferric salt begins to be reduced, the solubility of the resulting ferrous salt, although very small, enables the reaction between it and the chloroplatinite to proceed at once and to a more or less indefinite extent, depending upon the actual quantity of water present. For these reasons the prints made from improperly preserved papers are liable to be granular and flat. Platinum papers are therefore commonly stored in tin cylinders with caps which can be made air-tight by wrapping adhesive tape or a wide rubber band around the joint. In the cylinder there is also put a small package of anhydrous calcium chloride, so packed that none of the lime can sift out upon the paper in the cylinder. Calcium chloride, as it crystallizes from water solution, contains six molecules of "water of crystallization." When the crystallized salt is heated, at 200 degrees Centigrade it loses two-thirds of this water of crystallization, and upon further heating, until the dehydrated salt is melted, the remaining third is driven off, and the product is "anhydrous" calcium chloride. In this condition it has a very great affinity for water, so great that, when a little of it is exposed upon a saucer to the air, in a very short time by the absorption of moisture the salt becomes sticky and soon dissolves in the accumulated water. These reactions may be written:

1. Calcium chloride crystals
   = Calcium chloride (anhydrous) + Water
2. Calcium chloride (anhydrous) + Water
   = Calcium chloride crystals

It is by the application of the second reaction that platinum papers are preserved, since the lime salt is so much more hygroscopic than the iron and platinum salts of the paper that all moisture is seized and held by the calcium chloride. But there is naturally a limit to the quantity of water which can be absorbed by a given amount of calcium chloride. When this limit is approached, its efficiency as a dehydrating agent is much lessened, and of course when the limit is reached the effectiveness is gone. Therefore in storing platinotype paper it is necessary to consider the condition of the calcium chloride. If it has already absorbed much water, it can quickly be dehydrated by heating in an iron dish. Otherwise fresh anhydrous salt must be taken.

For producing sepia prints in platinotype, mercuric chloride is included in the sensitizing solution. The brown color of the image is due in some way to the mixture of platinum and mercury reduced by ferrous salt. There are both "cold bath" and "hot bath" sepia papers, the latter being developed in potassium oxalate solution at a temperature between 70 degrees Centigrade and 80 degrees Centigrade (160 degrees Fahrenheit to 180 degrees Fahrenheit). "Hot bath" sepias appear to be rather more permanent than the others, but both are naturally less so than the black papers which contain nothing else than pure platinum.

A sensitizer for "hot bath" sepia paper is prepared thus:

NO. 1

Ferric oxalate	40 grams
Oxalic acid	24 grams
Water, distilled, to	200 cubic centimeters

NO. 2

Potassium chlorate	0.4 gram
No. 1 solution, to	100 cubic centimeters

NO. 3

Potassium chloroplatinite	10 grams
Water, distilled, to	60 cubic centimeters

NO. 4

Mercuric chloride, saturated solution in distilled water	50 cubic centimeters

To coat a sheet of 20 inch by 26 inch paper, take 5 cubic centimeters of No. 1, 4.7 cubic centimeters of No. 2, 9.5 of No. 3, and 1.8 of No. 4. The paper, after printing, is developed in potassium oxalate solution of the same concentration as that used for the ordinary black process, 26 grams per 100 cubic centimeters, the temperature being maintained at 70 degrees Centigrade to 80 degrees Centigrade, as above noted, over a gas stove, or better on an electric hot-plate. The acid clearing-baths are used at half the concentration given for black prints, that is, 5 cubic centimeters of concentrated hydrochloric acid in each 600 cubic centimeters of the solution.

The many modifications to which platinotype is susceptible not only render the process one of much flexibility when used as a straight photographic method, but also adapt it especially to the use of the artist photographer. Besides the control which is given by variations in the constituents of the sensitizing solution, there are at least three forms of control which can be exercised over the print. In ordinary development the image appears instantly upon application of the oxalate solution. If the surface of the exposed sheet is first smeared all over with glycerine and the print is then brush-developed, as the worker may choose, with a mixture of equal parts of glycerine and developer or with the full-strength developing solution, the normal gradation of light and shade may be altered to any extent desired. The effect of the glycerine is a purely physical one, dependent upon the property of viscosity, in retarding the rate of development. Another mechanical process, for treating the completed print if it has been over-developed, consists in abrading the image, or such portions of the image as may require local reduction, with sawdust and water. A non-resinous sawdust is needed, and that from box-wood is the best. It is shaken up in water and the mixture is poured in a thin stream upon the gently inclined print, the latter being supported by pinning to a board. In this way the shadows may be lightened up and the darkened highlights cleared. The resultant effect has the quality of an engraving. The third method of control is chemical and is the same in principle as the toning processes which were discussed under silver printing. Although, as we have said, the platinum image is essentially a very permanent thing owing to the refractoriness of the element, yet it can be affected chemically by suitable reagents, and for the purpose in hand the same oxidizing agent can be used as is effective in toning the silver image, *viz.*, potassium ferricyanide. Just as in the case of silver, the platinum is oxidized and the ferricyanide is reduced to ferrocyanide. The toning solution contains also uranium nitrate and consequently insoluble red uranium ferrocyanide is precipitated upon the image. Since this is an intensifying operation, the print to be toned should in the first instance be printed light, and over-development is to be avoided. Brilliant red tones are secured by taking special care to free the paper from iron salts and to this end an extra clearing-bath or two is advisable:

NO. 1

Uranium nitrate	0.5 gram
Acetic acid (glacial)	3.0 cubic centimeters
Water, to	125 cubic centimeters

NO. 2

Potassium ferricyanide	0.5 gram
Acetic acid (glacial)	3.0 cubic centimeters
Water, to	125 cubic centimeters

Solution No. 1 may be made up in quantity as it keeps well, but No. 2 is unstable and must be prepared just before using. Mix the quantity of No. 2 given with an equal volume of No. 1 and dissolve in the mixture 0.1 gram of sodium sulphite. Leave the print in this solution until the tone is satisfactory, take it out quickly and sponge it, both front and back, with moistened absorbent cotton, and transfer it to an acid clearing-bath containing 5 cubic centimeters of concentrated hydrochloric acid in 600 of water. Pass the print on to a second acid bath, and wash for ten minutes, and, lastly, lay it upon clean muslin to dry. Blue tones may be had, from the same toning bath, merely by purposely failing to clear all the iron salt from the print immediately after development. Printing should in the first place be carried a little further than would give a normal black and white print. After development, the print is put for but ten seconds into the normal clearing solution and is then placed immediately in the toning bath until colored as desired. Clearing takes place in a solution of half the concentration used for red tones, *i.e.*, 2.5 cubic centimeters of hydrochloric acid in 600 of water. After clearing and washing the blue print is dried upon muslin, but on no account should the same pieces of cloth be used for both red and blue prints, as the quality of the red will be degraded. It is plain that the blue color is due to ferric ferrocyanide produced by metathesis between the ferric salt which is on the paper and the potassium ferrocyanide reduced from ferricyanide by the platinum. Success in the use of these toning methods depends wholly upon scrupulous cleanliness and the keeping of blue-toned paper away from the red.

A process practically identical in principle with platinotype is known as kallitype. Instead of platinum, the image is silver, produced by secondary reduction with ferrous oxalate, the primary image being formed in the iron salt, as is the case in platinum papers. It has been much complained of by photographers and in the photographic journals on account of its alleged lack of permanency. There is no possibility of doubt but that a silver print by the kallitype process may be made equally permanent with silver prints by any other method. When properly worked the process leaves an image in pure silver upon a substratum of pure paper, which is the condition essential to durability. Furthermore, the testimony of time may be advanced, for a certain kallitype print has hung upon the wall of an ordinarily illuminated room for upwards of seven years without appreciable alteration. Any worker who does not get both permanent results and exceptionally pleasing pictures with kallitype ought to test his chemicals thoroughly and, especially, examine carefully his methods of working, for somewhere in these he is sure to discover the cause. There is one characteristic of this printing medium which ought to make it interesting to a great many amateurs, its exceeding inexpensiveness. It is a fact that, including the cost of the chemicals, paper, developer and fixing salt, the completed prints need not cost more than ten cents per dozen for the 5 inch by 7 inch size. But the quality which it is possible to obtain in kallitype is not at all measured by this cheapness, for successful pictures can scarcely be told from platinum prints. Another advantage lies in the fact that negatives which no other silver process will print satisfactorily will yield excellent pictures in kallitype.

Any kind of paper may be used, with the same proviso as in platinotype, that the unsized varieties must be given a coat of sizing beforehand. The high grade drawing papers are particularly desirable; but for the beginner there is nothing more satisfactory than a good, heavy ledger paper, such as Weston's ledger, since it is already well sized, is very durable, and has surface which gives good quality in prints. As the operations of sizing the paper and coating it with the sensitizing solution are the same as in platinotype, and have just been described, we may pass at once to the preparation of the necessary solutions:

NO. 1

Ferric oxalate	30 grams
Water, distilled, to	150 cubic centimeters
Gum arabic, selected	3 grams

NO. 2

Ferric potassium oxalate	15 grams
Water, distilled, to	240 cubic centimeters

NO. 3

Oxalic acid	15 grams
Water, distilled, to	120 cubic centimeters
Ammonium hydroxide, concentrated	6 cubic centimeters

NO. 4

Potassium dichromate	7.5 grams
Water, distilled, to	120 cubic centimeters

All these solutions are to be made up and kept in chemically clean, dark brown bottles with tight-fitting glass stoppers. Besides this precaution, they should be put away in the dark. Number one is prepared by putting the measured quantity of ferric oxalate in the bottle, adding enough water, and shaking from time to time for half an hour. After it has stood in the dark for a day it will generally be found completely dissolved, and when this is the case the gum arabic is added and left to dissolve. The solution is then diluted up to the specified volume with water. It will keep for several months. The other three solutions need no comments. The sensitizing mixture for normal negatives consists of:

No. 1 solution	30 cubic centimeters
No. 2 solution	15 cubic centimeters
No. 3 solution	1.8 cubic centimeters
No. 4 solution	4 drops
Silver nitrate, *pure*	2.2 grams

About 2 cubic centimeters of the mixture are required to coat a sheet 11½ inches by 18 inches. Free nitric acid in the silver nitrate is detrimental and should be tested for with litmus paper beforehand. The salt may be purified by recrystallization, if necessary. Special sensitizers can be prepared for different kinds of negatives. For example, for very contrasty negatives, No. 4 may be omitted and No. 2 and No. 3 increased, and more silver nitrate added. Too great increase in the proportion of No. 3 induces fog. For negatives that are very soft and thin No. 4 may be increased, diminishing the quantity of No. 3, However, it is generally better to use a uniform sensitizer and exercise the necessary control by modifications in printing and development. The coated paper will keep in good condition for a month without any special precautions except against exposure to light. If it is desired to preserve it longer, it may be stored in the same way as platinum paper with anhydrous calcium chloride as a dehydrating agent.

After printing, which is similar to platinum, development is brought about in a solution of sodium acetate, variously modified according to the tone which is wanted. The acetate solution, 125 grams of the salt dissolved and diluted to one liter, can be made up in bulk, as it works best when a day or two old. For warm blacks, take:

Acetate solution	240 cubic centimeters
Tartaric acid	0.75 gram
No. 4 solution	0.6 to 6.0 cubic centimeters

The longer the exposure or the flatter the negative, the greater should be the proportion of No. 4 solution used, as potassium dichromate appears to act somewhat as a restrainer. For platinum black tones take:

Acetate solution	240 cubic centimeters
Tartaric acid	1.5 gram
Phosphoric acid (50 per cent.)	1.2 cubic centimeters
No. 4 solution	0.6 to 3.0 cubic centimeters

To make sepia prints with kallitype, the developer contains borax and Rochelle salts:

NO. 5

Water, distilled, hot, to	1000 cubic centimeters
Borax, powdered	37.5 grams
Sodium-potassium tartrate ...	75 grams

NO. 6

Sodium-potassium tartrate ...	75 grams
Water, distilled, to	1000 cubic centimeters

In making up No. 5, dissolve the borax in the hot water, let it cool, and finally add the tartrate, and dilute to one liter. Sepia tones are obtained by mixing these solutions in the proportion of one part of No. 5 to three parts of No. 6, and adding No. 4 solution as required.

Kallitype prints must be both cleared of iron salts and fixed in thiosulphate solution, and it is in the last operation that the process differs from platinotype. The kind of clearing-bath to use depends upon the developer. Following immersion in sodium acetate solution, prints are cleared in a bath, made fresh each time:

Sodium citrate	7.5 grams
Citric acid	1.5 gram
Water, to	250 cubic centimeters

After the borax and Rochelle salts developer, use a solution of Rochelle salts, 75 grams to the liter of water, to which are added 7.5 cubic centimeters of No. 4 solution. Leave the prints in this bath for ten minutes. After coming out of the clearing-bath, they must be thoroughly washed to free them from all traces of acid, since this would cause decomposition of the thiosulphate fixing bath which follows. They are then fixed for ten minutes in:

Sodium thiosulphate	25 grams
Water	500 cubic centimeters
Concentrated ammonium hydroxide	5 cubic centimeters

and given a final thorough washing until all thiosulphate has been removed. After this the prints are dried, best between lintless photographic blotters, to keep them free from dust.

In this chapter the attempt has been made principally to give an outline of the processes with ferric salts, showing as simply as possible the rationale of the methods and describing in an elementary way the chemical reactions upon which they depend for making technically successful prints. It is possible that some readers, at least, may become sufficiently interested to wish to pursue the subject further. Such may find in the accompanying bibliography full and practical accounts for handling these fascinating and beautiful photographic media.

CHAPTER X

PRINTING PROCESSES WITH CHROMIUM SALTS

ORGANIC colloids, such as gelatine, gum arabic, etc., have the property of combining with chromium salts (in which the element is positive, or basic), with mercurous chloride, tannic acid, and various resins. The reaction is apparently not a photochemical one, and its product is the colloid so altered by the chemical admixture of chromium salt, to take an example, as no longer to be soluble in water. That this insoluble compound has photo-chemical properties is shown by the fact that, if it is not exposed to light, it is able to combine with water, becoming hydrated and swelling, as the water is absorbed, in a similar manner to the original, uncombined colloid; whereas after it has been exposed, not only is it still insoluble, but it refuses to absorb any water, that is, does not become hydrated. When the colloid, however, is mixed with a chromate (usually a dichromate)and kept in the dark, no insolubilizing action takes place. If the solution is coated upon paper, and not exposed to light, it will quickly be dissolved and washed off by warm water. But by the action of light upon the mixture, reduction of the chromium, on the one hand, and partial oxidation of the colloid, on the other, occur; and these reaction products are chemically combined, forming the insoluble, non-absorbing end-product of colloid-chromium salt. The oxidizing action of chromates upon organic compounds is well illustrated by the accompanying experiment.

Experiment 34. Acidify with hydrochloric acid 5 or 10 cubic centimeters of dilute potassium dichromate solution, heat the liquid to boiling, add a little ethyl alcohol, and continue the boiling. The gradual change in the color of the solution from orange to green indicates the reduction of the chromate to chromic chloride; and at the same time the pungent odor of aldehyde shows the oxidation of alcohol. Reaction:

Potassium dichromate + Ethyl alcohol
+ Hydrochloric acid
= Chromic chloride + Potassium chloride + Ethyl
aldehyde + Water

In chromic acid and its salts, such as the dichromate for example, the chromium atom forms part of the acidic or negative portion of the molecule; but in such compounds as chromic chloride, chrome alum, etc., chromium is in the basic or positive part. Reduction of a chromate, therefore, as illustrated above, consists in changing the chromium atom from the negative part of the compound to the positive part, as well as in removing oxygen from it. We are now ready to experiment with the action of light-reduced chromium salt upon gelatine.

Experiment 35. Soak up in enough cold water 20 grams of gelatine and get it into solution by warming. In a weak light dissolve in this 6 grams of potassium dichromate and dilute up to 100 cubic centimeters. Coat some of this sensitive mixture upon several small pieces of paper and dry them. Expose three of these under a contrasty negative, giving full exposure, and treat them severally as follows:

(1) Place one of the prints in hot water. The gelatine dissolves off from the paper in proportion as it

has been protected from the light, but, wherever light has acted, more or less gelatine has become insoluble and non-absorbent, according to the amount of the light-effect.

(2) Put a second print into cold water and observe that the areas which were protected from light by the dense parts of the plate swell, by the absorption of water, the light-affected portions being unchanged.

(3) Spread upon the third exposed paper some thin printers' ink, soak it for a time in cold water, and then gently wipe the surface with a wet sponge or wet absorbent cotton. Upon those areas which were affected by the light, since they have been rendered non-absorbing, the ink adheres. From the other parts it is removed according to the amount of water absorption, which is proportional to the photo-chemical effect.

In these simple experiments we have the basis of all the processes which depend upon the dichromatizing of colloids, and we must now try to make clear not only what happens in the photo-chemical reaction, but exactly what conditions prevail at the end of the reaction in the thin layer of medium spread upon the surface of the paper. When gelatine and a chromic compound are mixed they combine, as we have previously noted, and an insoluble product results which is water-absorbing, if unexposed, but non-absorbing after exposure. This reaction may perhaps be expressed in the following way, in the absence of light:

Gelatine + Potassium-chromic sulphate
= Gelatino-chromic sulphate + Potassium sulphate

A mixture of gelatine and a salt of chromic acid, almost insensitive in solution, or before the paper is dry, when dehydrated appears to form a photo-sensitive compound. It is certain that the dried mixture, as we learned in the experiment, is sensitive. The combination may perhaps be represented thus:

Gelatine + Potassium dichromate
= Gelatino-potassium dichromate

By light, this complex compound is so altered that hydrogen is abstracted from the gelatine portion (oxidation) and oxygen from the chromium part (reduction), and the final product is both insoluble and a non-absorbent of water:

Gelatino-potassium dichromate + Light
= Oxidized-gelatino-chromic oxide + Potassium hydroxide

At all events, it is practically certain that the partially oxidized gelatine and the reduced chromium compound are in chemical combination in the end. The conditions prevailing in the sensitive gelatino-dichromate film during the exposure can now be considered. Let us in imagination isolate one ray of the white light and allow it to fall upon different portions of the negative at will. When it is directed upon an area of clear glass, the instant it reaches the gelatine surface, absorption of its energy commences and the photo-chemical change is initiated. Consequently, as the layer of gelatine immediately beneath the surface is met, there is a diminished amount of light-energy applied to it, and so on, through layer after layer, until either the film is entirely passed through or the light-energy is wholly absorbed. Of course, it must be understood that it is the energy of the photo-chemical, or actinic, wave-lengths of which we are speaking. In the case of the yellow dichromated gelatine the energy of the actinic wave-lengths is rapidly used up, that is, the light is able to penetrate but a few layers before being completely absorbed. In areas partially shaded by thin deposits of silver, much of the light has already been absorbed by the negative before arriving at the gelatine surface of the paper, therefore the depth to which its influence extends in the film is less, in proportion to the amount of absorption by the negative, than in the unshaded parts. If in any regions the silver deposit of the plate is sufficiently dense to absorb all actinic wave-lengths, no effect upon the gelatine is produced. Dichromated gelatine is sensitive to longer wave-lengths than are the silver salts, and its maximum occurs in the blue-green. Since most of the photochemical action is caused by the blue rays, it will be clear that only a very thin layer of film can be affected under the best conditions of exposure and that but little preliminary absorption by the silver image makes marked differences in the depth to which the light-effect penetrates. Usually the whole of the surface layer of gelatine-coated paper is insolubilized and the still soluble portions are consequently enclosed between this layer and the paper support, where they are protected from the water in which the prints are developed, as was remarked in Chapter III.

This brings us naturally to the subject of carbon printing, for the situation just described is the cause of the marked difference between the manipulation of carbon and that of silver and platinum prints. The principles which have been outlined in the preceding chapters are applied, in the carbon process, as well as in the other colloid-dichromate methods, by incorporating with the gelatine-dichromate mixture a permanent pigment in suitable proportion. This coloring matter may be the form of carbon known as "lamp-black," or it may be almost any water-color pigment desired. The photographic image is formed by the finely divided particles of this pigment embedded in insolubilized gelatine, since in all parts of the sensitive film where the gelatine remains soluble, owing to its not having been acted upon by light, the washing away of the gelatine removes also the pigment, but wherever the gelatine is insoluble it firmly retains the coloring material. In working the carbon process it is scarcely to be recommended that the amateur attempt the preparation of "carbon tissue," as it is called. A much better and more uniform, and therefore more satisfactory, product can be purchased from the dealers. These tissues come provided with the gelatine-pigment film in a very considerable range of colors and either cut to size or in rolls. Before printing they are sensitized by immersion of the tissue in a solution of dichromate, and dried in the dark:

Potassium dichromate	15 to 30 grams
Ammonium carbonate	1.5 grams
Water, to	1000 cubic centimeters

The proportion of dichromate is varied to suit climatic conditions, less being used in summer, or in a warm climate, than is needed in winter, or in a cold climate. The function of ammonium carbonate is to aid in preserving the gelatine from becoming spontaneously insoluble, and it is slightly variable in amount. Less may be used in cool, dry weather, and more if it is damp. Alcohol, or a mixture of alcohol and ether, is sometimes recommended to be added to the sensitizing solution to secure rapid drying in hot weather when the humidity is high. Such a formula is the following:

Potassium dichromate	30 grams
Ammonium hydroxide, concentrated	0.75 cubic centimeters (about 12 drops)
Water	700 to 800 cubic centimeters

To this add a mixture of ethyl ether, 30 cubic centimeters, and ethyl alcohol, 15 cubic centimeters, and make up the solution to 1,000 cubic centimeters with water. Keep all sensitizing solutions away from the light.

When sensitized, care has to be taken that no actinic light reaches the tissue, as it has been found that once the reaction is started by light it will proceed slowly even in the dark; and for this reason when carbon tissue is exposed it is at once developed. If it be under-exposed, however, and put away in the dark for a suitable length of time, on account of this continuing action a normal print will be developed up. No visible image is formed in printing, so that the exposure is regulated by actinometer. In order to develop the printed tissue by washing away the soluble portions of pigmented gelatine, since these soluble layers lie between the insoluble upper surface and the paper backing, it is necessary to remove the backing. This operation is performed by putting into cold water the exposed tissue and with it either a sheet of "single transfer" paper or waxed "temporary support" according as the picture is to come out finally reversed as to right and left, or unreversed. The transfer paper has a gelatine coating upon one side and this is placed face to face with the tissue. Both are drawn together from the water and are firmly squeegeed into contact, all air and water being expelled from between them. The united sheets are next put between blotting papers under pressure, and left from a quarter of an hour to over an hour, depending upon the pressure used and the character of the paper's surface, in order that the tissue and transfer paper may adhere together uniformly. As soon as the dichromate in the tissue penetrates to the back of the transfer paper, staining it yellow, development may be undertaken. This part of the process consists merely in a preliminary soaking of the combined papers in water at a temperature between 32 degrees Centigrade and 38 degrees Centigrade. The gelatine around the edges presently begins to dissolve. After a few minutes longer, put the papers into a second tray of water, arranged to be kept at a temperature from 38 degrees Centigrade to 48 degrees Centigrade, and in a minute or two, beginning at one corner, strip off the tissue. The print, which is now to be left upon the transfer paper, must be held under the surface of the water during this process of stripping. By rocking the tray, the solvent action of the warm water is caused to begin removing the soluble gelatine, and details commence to appear in the picture. Development is completed from this point by laying the print face up on a plate of glass inclined over the tray and gently pouring the warm water over it with a cup. The print dries slightly darker than it looks when wet, so it is developed to a little lighter tint than is desired in the final picture, and is placed in cold water as a stop-bath. After this it is allowed to soak in a five percent. solution of potassium aluminum sulphate ("alum") for ten minutes up to an hour, according to the thinness or thickness of the paper, and is lastly washed in running water for half an hour. If right-and-left reversal is not objectionable, as in pictorial work and some portraiture, and the "single transfer" paper has been used, the picture is finished by drying. Otherwise the "double transfer" method will have been employed, and the thoroughly washed print has finally to be transferred again, from the "temporary support," to the final support on "double transfer" paper. This paper, also gelatine-coated, is given a preliminary soaking in water at 32 degrees Centigrade to 38 degrees Centigrade to soften up the gelatine, and is afterwards put, together with the print, into cold water. Face together, the two are withdrawn from the tray, avoiding air-bubbles, then they are squeegeed into contact and hung up to dry. When thoroughly dried, in six hours or so, the two papers are separated at one corner and stripped apart. The gelatine image leaves the waxed surface of the "temporary support" and sticks permanently to the final support, upon which it is dried. In this way a non-reversed picture is obtained. Waxing of the "temporary support" is accomplished by spreading with a tuft of cotton upon the gelatine surface a solution of 20 grams of yellow resin and 7 grams of beeswax in 400 cubic centimeters of turpentine. Afterwards it has to be polished, with a larger wad of cotton, and when all the turpentine has evaporated the paper is ready for use. If carbon prints are made from enlarged negatives, the process can be simplified by making the enlargement a reversed negative, when the "single transfer" method will give a non-reversed picture. The published accounts and descriptions of carbon printing all sound, in the reading, much more complicated than the process actually is. This fact, together, perhaps, with the seemingly unorthodox bandying about of the photographic image, turning it upside down for development and putting it back right-side up again, has probably deterred a great many amateurs from experimenting with it. This is unfortunate, for, even if we admit the charge of greater complication, one really well-executed print in carbon, or in gum, is worth a whole handful of the usual developing-out prints which so many amateurs seem to be fond of turning out wholesale. The point to be established here is not that beautiful pictures are impossible in silver, whether on printing-out or on developing-out papers, for they are not impossible, but that by reason of the widely advertised simplification of photography for the amateur, the art has become too automatic and stereotyped. All his thinking and study have been performed for him by the manufacturers. The real photographic education of the amateur generally begins only when he takes up one or other of the individualistic printing methods, platinum, carbon, gum, etc., and endeavors to express something in his pictures.

Printing in gum, or gum-bichromate as it has been called, is founded on the same principles as carbon, since it is, in fact, a variation of the carbon process. A mixture of gum arabic, potassium dichromate, and pigment is coated upon paper, dried, exposed to light, and washed in water and dried. The result, if successful, has a distinctiveness which has commended the method to the best pictorialists the world over. In working gum, the photographer theoretically can acquire absolute command over the process, since the choice of paper and pigment is entirely under his control, the proportions in which they may be put together with the colloid can be varied to suit his requirements, and the development process may be such as to allow unlimited scope to his artistic abilities. It is not a complicated process, at least in single printing; requires no transfer of the colloid-pigment image; is capable of giving as fine prints as any other method (some think finer); and withal is so exceedingly inexpensive that the amateur can experiment with it without stint. If he is so unfortunate as to fail to get satisfactory pictures in the end, he can console himself with the thought that he is out little besides the time spent. But there is no need for anyone to fail, for various methods have been published for the gum print, and it is necessary only to study out carefully the reasons for the different manipulations and then apply patience and pains in performing them for oneself in order to make prints that at the very least will bear inspection.

The essential materials for working in gum are four in number, paper, which may be of different weights, surfaces, and textures, but must be sufficiently tough to withstand soaking in water; gum arabic, suspended in a muslin bag in cold water in the proportion of 40 grams of the gum to 60 cubic centimeters of water, and to which is added formaldehyde 10 drops for each 100 cubic centimeters, or 0.02 gram of mercuric chloride; a saturated solution (at ordinary temperatures) of potassium dichromate kept in a brown bottle; and, for the beginner, two or three pigments such as lampblack, burnt sienna, and burnt umber, or, for the advanced worker, in addition to the foregoing, ivory black, Indian red, Venetian red, Indian yellow, permanent blue, cobalt blue, madder lake, and emerald oxide of chromium, etc. Only permanent colors should be selected, and on this account the aniline dyes are discarded. It is immaterial whether the pigments are in water-color tubes or in powder form, the advantage of cheapness being with the latter. Of this list of colors, lamp-black, ivory black, burnt sienna, Indian yellow, cobalt blue, madder lake, and emerald oxide of chromium are transparent; burnt umber, Venetian red, and permanent blue are semi-transparent; and Indian red is opaque. Besides these four essentials there are several accessories needed. For coating the emulsion upon paper, the best method is by use of the "air-brush." It gives the most uniform coating, without streaks or brush-marks, and by it the whole sheet is coated, without being cut up. In lieu of this desirable implement, ordinary brush-coating will do. Use a flat brush that is soft and thick and about four inches in width, or narrower for smaller sizes of paper, and even up streaks, etc., by blending with a three- or four-inch flat badger blender. The coating mixture is made by grinding the ingredients together in a mortar with a capacity of about 200 cubic centimeters. To make this mixture, put about equal quantities (by volume) of pigment and gum solution into the mortar and grind them together with the pestle. If any of the pigment fails to be taken up by the gum, add just enough more of the latter to take up in suspension the rest of the former. In this way the gum and pigment are to be balanced against each other, there being an excess of neither. Complete the mixture by the addition of approximately four to six times the bulk of gum-pigment of the saturated dichromate, mix thoroughly in the mortar, and strain through muslin. Coat and dry the paper, and, if it is to be kept any length of time, avoid exposing it to any actinic light after it becomes dry. So long as it is wet, it remains insensitive, but it becomes about as sensitive as platinum paper as soon as the moisture is removed, and, on account of the continuing action that has previously been described, even short exposure to actinic light in this condition produces after a time general fog when development takes place. The sensitized paper will keep for some days in good condition if unexposed and stored where it will be thoroughly dry. The exposure of paper, coated as described, is a simple matter if pigments other than browns and blacks are used, since the paper prints out. Give a full printing to bring out all detail and gradation. When using browns and blacks, of course there will be no visible image, and the printing time has to be determined by actinometer. Development is performed by means of wet blotting-paper of the photographic quality. First soak the cut-to-size blotters thoroughly so that all bubbles of air may be expelled. Lay down a clean sheet of glass the same dimensions as blotters and prints, and upon it put one of the wetted blotters. Soak the prints for a few minutes in cold water, separately, and put one face down upon the wet blotter, the second one face up upon the first, then another wet blotter and two more prints back to back, and so on until all the prints are in the pile, with a blotter upon the top, and finished off with a second plate of glass. Cover the entire pile with water in a sufficiently deep dish and allow the developing process to go on automatically. The length of time required will depend upon depth of printing, prints that have been most fully exposed developing slowest. Lightly printed paper may be completely developed in an hour or so. Consequently, until one has acquired the knack of judging beforehand about when his prints will be ready, it will be well to examine them after about an hour. This task is done by taking the whole pile of glass, prints, and blotters in one body from the water and, resting it on one corner, letting it drain for several minutes until the superfluous water has run away. Take down the pile, setting it up again in the reverse order as fast as it comes down, but removing and drying any prints that appear to be fully developed. They will dry a trifle darker than they appear when wet. Then put the unfinished ones, in the pile, back to soak, and examine again in an hour, or longer if they were thought to need more time than that. Prints will sometimes be put to soak without being examined, needing no attention in the interim, over night, or for twenty-four hours. The blotting-paper can be used over again, up to three times, if it is not permitted to dry until the absorbed gum has been washed out, and it is then kept from the light. The method here briefly outlined is due to Mr. Walter Zimmerman, to whom photographers both professional and amateur are indebted for many helpful suggestions besides his excellent gum process. A much more complete and detailed account of it is given in the *Photo-Miniature*, Number 113, "Gum-Bichromate Printing," which the reader is earnestly advised to study.

There are several interesting modifications of colloid-dichromate methods, two of which are the inventions of Mr. Thomas Manly. In the ozotype process a gelatine film impregnated with dichromate, manganous salts, alum, and boric acid is prepared upon paper and dried in the dark. The mixture of alum and boric acid acts as a preservative. By the effect of light in the reduction of the dichromate, manganous salt is oxidized to the manganic state and the image, which is visible and of a brown color, is considered to be composed essentially of manganic oxide. This image is merely intermediate and does not form the completed picture. The final print is made by putting a sheet of carbon tissue of the desired color into an acetic acid solution containing an organic reducing agent, magnesium and ferrous salts, and bringing the face of this tissue into contact with the paper carrying the manganic oxide image. In the presence of acid manganic oxide is reduced, by the ferrous salt and the developer (hydrochinon), to the manganous condition, and the gelatine of those portions of the carbon tissue which are in contact with the manganese compound, of which the image consists, becomes insoluble. The papers are subsequently separated in water at 43 degrees Centigrade and development carried out in the ordinary way by dissolving the soluble parts of the gelatine. Since the pigment-carrying gelatine of the carbon tissue is finally left upon the surface of the printed sheet, there is no right and left reversal of the image, and this is one of the advantages of the process. Others are found in the visibility of the image during printing, and the brush control of development which is common to the pigmented gelatine methods. In 1905 Mr. Manly brought out his ozobrome process, using bromide prints, instead of light shining through negatives, for making the exposure. By this means the worker is made independent of daylight and enjoys the advantage of not requiring enlarged negatives. The image either can be formed upon the bromide enlargement directly or is transferable to another support and is non-reversed in both cases. The second method is generally preferable because then the bromide can be used over again to make other ozobrome prints. If carefully handled also it may be entirely uninjured in the end. The peculiar feature of the process is that the pigmented gelatine film is so treated chemically that a contact exposure of it to the silver image of a bromide print for twenty minutes produces an insoluble gelatine-pigment image upon the ozobrome tissue, which is adaptable to the usual forms of development with hot water.

In the bromoil process photography seems to have been carried to its extreme in the way of control, for the pigment is applied with a brush. A vigorous bromide enlargement is prepared, the silver image is oxidized by ferricyanide and removed by solution in thiosulphate and washing. At the same time the portions of the gelatine film originally occupied by the metallic image are insolubilized by reduction of dichromate so that there is substituted what may be called a latent image in insoluble gelatine which is ink-absorbing. The surrounding gelatine is water-absorbing and therefore refuses to "take up" ink. The latter is put upon the print by gently dabbing with a soft brush, and obviously its amount and its distribution are wholly at the command of the worker.

These last pigment processes are distinctly ultra-advanced methods suited to the worker of more than usual artistic gifts and attainments. They are indeed photographically based, but their chief dependence for success is, after all, not so much upon the control of delicate chemical and physical reactions as upon the worker's technical skill with the brush and his personal powers of expression.

CHAPTER XI

THE CHEMICALS OF PHOTOGRAPHY

WE have employed the metric system of measures in this book up to the present point without any attempt at its justification. It does not, in fact, seem likely that it will need to be justified in the minds of the majority of readers, even though it be true that most photographic formulas are still given in English units for English and American workers, and even though this majority may still weigh out its photographic chemicals by grains, scruples, and ounces. But if justification be required in the minds of some and in the practice of many more, it ought to be sufficient to say that since the use of the metric system has been found to simplify things materially for the scientific investigator, it will certainly be to the advantage of the photographer to adopt it. On this account all the experiments and all the formulas given in this book have been written in metric units exclusively, since undoubtedly these units will be familiar enough to the more advanced readers, and any readers who have not previously been acquainted with them will quickly become so in the course of the experiments. Very fortunately it is coming to be the practice to express formulas in both English and metric units in many of the journals and other publications, so that we may expect soon to find the former measures left out altogether. Nevertheless, if any one insists upon making use of his apothecary and avoirdupois weights, he can convert the metric amounts into the old system by use of the conversion tables in the appendix. Let us hope, however, that the simplest way out has been adopted by every reader, namely, by the purchase of a set of metric weights at the start.

Most photographic operations depend upon having the necessary substances in solution in water, as, for example, the developer solution, which acts upon the latent image by first dissolving it piecemeal and immediately reducing and depositing the silver before it has an opportunity to get away; or the intensifying mixture, which dissolves out a little of the silver image and puts in its place some more non-actinic material. So there are two things at least which it is needful to know about every solution, first precisely what are its components, and second what are the concentrations of these constituents. Frequently also the temperature of the solution is important and this is told by the thermometer. There are two ways in which the concentration of a dissolved substance can be expressed, and in both cases the matter is exceedingly simple if metric units are employed, but not nearly so simple with the English units. As we have shown in some of our experiments, solutions may be made up in percentages, 10 grams of sodium chloride dissolved in water and diluted to 100 cubic centimeters forming a 10 percent sodium chloride solution. It is well to note that by dissolving 10 grams of the solid in exactly 100 cubic centimeters of water there is not made a 10 per cent solution for the reason that the resulting volume will in such a case be a little different from 100 cubic centimeters. Taking a suitable volume of the 10 per cent solution and diluting, it is a very easy matter to prepare solutions of any desired percentages less than ten. The simplicity of this proposition comes from the established relation between the gram weight and the cubic centimeter of water, one cubic centimeter of liquid water, at all temperatures, weighing very nearly (although not quite exactly, except at + 4 degrees Centigrade) one gram. There is no such simple relation found in the English system. The second method of expressing the concentration of a substance in solution is based upon either the molecular weight of the substance or upon its equivalent weight. In this way solutions are prepared which, volume for volume, are chemically equivalent to one another, and this becomes very convenient for the chemical experimenter. Thus, the molecular weight of sodium chloride is 58.46; by dissolving 58.46 grams of pure sodium chloride in distilled water and diluting as exactly as possible to one liter, we should have a normal solution of sodium chloride, as it is called. In a similar way, 169.89 (the molecular weight) grams of silver nitrate in one liter of solution will make a normal solution of silver nitrate; and by mixing together one liter of normal silver nitrate with one liter of normal sodium chloride there would be formed 143.34 (the molecular weight) grams of silver chloride. So also a thiosulphate fixing solution at 20 per cent. concentration is very closely 0.8 normal, since the molecular weight of sodium thiosulphate is 248.22, and a normal solution would contain that number of grams per liter.

To illustrate the concentration of the substances present in a developer, we may take a hydrochinon formula essentially as given by Schering, thus:

Sodium sulphite, dry.........	20.5 grams
Hydrochinon...............	4.7 grams
Potassium carbonate, dry.....	65.7 grams
Water, to..................	1000 cubic centimeters

A normal sodium sulphite solution contains 63.04 grams per liter; and normal potassium carbonate, 69.10 grams of the salt per liter. At present it is impossible to express the concentrations of most developing agents in terms of normal solutions because chemical research has not so far determined quantitatively the reactions between the developing agents and the silver salt of the plate. Until these quantities have been measured, the concentrations can very well be expressed in terms of the gram-molecular weights. Thus a solution of hydrochinon containing 110.02 (the molecular weight) grams per liter may be called a "gram-molecular solution" (G.-M.S.). Therefore the Schering formula when translated into molecular weight concentrations becomes practically (N meaning normal):

Hydrochinon	0.043 G.-M.S.
Sodium sulphite	0.32 N.
Potassium carbonate	0.95 N.

Another developer frequently used is the so-called Wellington Pyro-Soda in two solutions:

NO. 1

Pyrogallic acid	100 grams
Sodium sulphite, dry	100 grams
Citric acid	8.3 grams
Water, to	1000 cubic centimeters

NO. 2

Sodium carbonate, dry	40.4 grams
Sodium sulphite, dry	54.5 grams
Water, to	1000 cubic centimeters

For use, 4 cubic centimeters of No. 1, 30 cubic centimeters of No. 2, and 30 cubic centimeters of water are mixed. When diluted for use in developing, the solution has the following concentrations:

Pyrogallic acid	0.05 G.-M.S.
Sodium sulphite	0.50 N.
Citric acid	0.01 N.
Sodium carbonate	0.35 N.

Since normal solutions are all equivalent to one another, and the same is true of 0.1 normal solutions, etc., we can at once compare the strengths of solutions when they are expressed in the fractional normal form. It is seen at a glance that the concentration of sodium sulphite in the Wellington formula is nearly double that of the other; whereas the concentration of carbonate is only about one third. The reason for these differences in concentration will be plain if we recall the density-giving properties of hydrochinon and the characteristics of pyrogallic acid, *viz.*, its propensity to dyeing the gelatine, and its oxygen-absorbing activity when in alkaline solution.

At first sight it may seem that this system of making up solutions is complicated and abstruse. We shall show in a very few words not only that this is not at all the case, but that, on the contrary, it is the simplest and easiest method in practice, if metric units be adopted. Let us keep in mind, first, that a normal solution, or a gram-molecular solution, of any substance signifies a solution containing a definite number of grams in a volume of one liter; and, second, that this definite number of grams is always either the whole molecular weight or some fraction of the molecular weight of the substance. So in order to make the preparation of normal or fractional normal and gram-molecular solutions a simple matter, all that is necessary to have is a list containing these definite weights per liter for all the substances we wish to use. Such a list we have already started, and it will be well to tabulate and extend it here. Further molecular weights will be found in the tables at the end of this chapter.

1.0 N. potassium carbonate	69.1 grams anhydrous salt per liter
1.0 N. sodium carbonate	53.0 grams anhydrous salt per liter
1.0 N. sodium sulphite	63.0 grams anhydrous salt per liter
1.0 N. potassium bromide	119.0 grams per liter
1.0 N. potassium disulphite	55.5 grams per liter
1.0 G.-M.S. amidol	197.0 grams per liter
1.0 G.-M.S. duratol	199.1 grams per liter
1.0 G.-M.S. hydrochinon	110.0 grams per liter
1.0 G.-M.S. metol	344.3 grams per liter
1.0 G.-M.S. pyrogallic acid	126.0 grams per liter

Assuming that 3.0 normal solutions have been prepared of sodium carbonate and sodium sulphite, by dissolving 159 grams and 189 grams respectively, and diluting each to 1,000 cubic centimeters, and that we wish to make up 100 cubic centimeters of pyro-soda developer to use immediately, we should take, referring to the fractional normal formula for this developer given on page 172, 12 cubic centimeters of 3.0 normal sodium carbonate, 17 cubic centimeters of 3.0 N. sodium sulphite, 1 cubic centimeter of 1.0 N. citric acid (70 grams per liter), and add 0.6 gram of pyrogallic acid (100 cubic centimeters is 0.1 of one liter, and therefore a 0.05 G.-M. solution will have 0.1 × 0.05 × 126.0 grams, or 0.6 gram of pyro in 100 cubic centimeters of solution), after which this mixture is to be diluted with water up to a volume of 100 cubic centimeters. The three-times normal carbonate solution may be made up in quantity, if it is kept in a bottle having a tight stopper to prevent alteration of the concentration by evaporation. A rubber stopper is best for this bottle. If it be desired to make up considerable amounts of three-times normal sodium sulphite, the solution should be put in a number of smaller sized, full bottles with tight-fitting stoppers. The concentration of sulphite solutions will change not only by evaporation, if precautions are not taken, but also from spontaneous oxidation by the air. A good plan to follow is to make up only a half liter or a liter at a time, according to the amount of work that is being done, since sodium sulphite keeps much better in solid form than it does in solution. More of these standard developer formulas, in the fractional normal form, will be found in the appendix. The advantages of this system are numerous: it has both simplicity and uniformity; a variety of different developers can be easily had on hand and used without cumbering the darkroom and its cupboards with a great array of bottled developer solutions; the concentrations can be quickly varied by definite amounts, if one be given to experimenting; and it is economical, because there are never any prepared solutions standing around to become oxidized and thus wasted, if the photographer takes a few weeks' vacation from his hobby. When a particular formula has been selected for permanent use, the proper amounts of developing agent to make the desired volume of solution can be weighed out and put up in cork-stoppered vials. A supply of these kept on hand will be found very convenient.

For containing solutions in bulk it is desirable to have a supply of 0.5 liter, liter, and 2 liter glass-stoppered bottles, and to use them in the following way for making up solutions. Take one of them, say a 2 liter bottle, and measure into it carefully with a graduate 1,000 cubic centimeters of water. Stick upon the side of the bottle across the water-level a label and mark on this the level of the surface, preferably in indelible ink. Do the same for the 2,000 cubic centimeter level; and similarly for the other bottles. If 2 liters of a solution are required, dissolve in enough water contained in a beaker or other convenient dish the weighed solid, filter this solution upon filter paper in a funnel supported in the neck of the bottle, pour a little water upon the filter after the solution has run through to rinse off the paper, and, after this also has run into the bottle, make up to the mark on the label with water, and mix the liquid thoroughly by shaking the stoppered bottle. Write upon a larger label gummed to the bottle the name of the solution, *i.e.*, "3.0 N. Sodium Carbonate," for example. This is a general method for preparing solutions, to dissolve the solid, or solids, in a portion of the required water, then to filter, if necessary, and finally to dilute up to the specified volume with water. Sometimes the solids have to be dissolved in a particular order to avoid precipitation, as is the case with duratol-hydrochinon developer.

It is frequently useful to have at hand prepared solutions of acids and alkalies of known approximate concentrations. Subjoined are data for making up such solutions.

1. Acetic acid, concentrated, 99.5%, 17.5 N; acetic acid, dilute, 5. N, 71 cc. of the concentrated acid diluted with water to 250 cc.
2. Ammonium hydroxide, concentrated, 28%, sp. gr. 0.90, 7.3 N; ammonium hydroxide, dilute, 7%, sp. gr. 0.97, 2. N, 18 cc. of the concentrated ammonia diluted to 250 cc. with water.
3. Hydrochloric acid, concentrated, 39%, sp. gr. 1.20, 12.8 N; hydrochloric acid, dilute, 20%, sp. gr. 1.10, 6. N, 46 cc. of the concentrated acid diluted with water to 250 cc.; hydrochloric acid, dilute, 10%, sp. gr. 1.05, 3. N, 22 cc. of the concentrated acid made up with water to 250 cc.

4. Nitric acid, concentrated, 70%, sp. gr. 1.42, 16. N; nitric acid, dilute, 40%, sp. gr. 1.25, 8. N, 88 cc. of the concentrated acid diluted with water to 250 cc.; nitric acid, dilute, 25%, sp. gr. 1.15, 4.4 N, 50 cc. of the concentrated acid made up to 250 cc. with water.

5. Sulphuric acid, concentrated, 96%, sp. gr. 1.84, 18. N; NEVER POUR WATER INTO CONCENTRATED SULPHURIC ACID; sulphuric acid, dilute, 60%, sp. gr. 1.50, 9. N, 122 cc. of the concentrated acid poured, a little at a time, slowly and carefully, with thorough cooling of the mixture during the operation, into cold water, and, when cold, made up to 250 cc.; sulphuric acid, dilute, 33%, sp. gr. 1.25, 4. N, 56 cc. of the concentrated acid made up, as above, to 250 cc. with water.

Photographic Chemicals

1. Acids and Ammonia

Name	Formula	Molecular Weight	Grams in 100 cc. of Solution			Solubility. in Grams per 100 g. of Solution		Common Name
			Sp.gr.	Temp.	Weight	Temp.	Weight	
Acetic acid	$HC_2H_3O_2$	60.032	1.058		105.3			Acetic acid
Boric acid	H_3BO_3	62.024				20°C	3.85	Boracic acid
Citric acid	$H_3C_6H_5O_7 \cdot H_2O$	210.08				25°	64.8	Citric acid
Hydrochloric acid	HCl	36.468	1.20	15°C	46.9			Muriatic acid
			1.10	"	22.0			
			1.05	"	10.7			
Nitric acid	HNO_3	63.018	1.42	"	99.1			Nitric acid
			1.25	"	49.8			
			1.15	"	28.6			
Oxalic acid	$H_2C_2O_4 \cdot 2H_2O$	126.048				20°	8.07	Oxalic acid
Phosphoric acid	H_3PO_4	98.064	1.71	"	145.4			Phosphoric acid
			1.35	"	67.5			
Sulphuric acid	H_2SO_4	98.086	1.84	"	176.6			Oil of vitriol
			1.50	"	90.0			
			1.25	"	41.3			
Tartaric acid	$H_2C_4H_4O_6$	140.048				20°	139.44 g. per 100. g. wate .	Tartaric acid
Ammonium hydroxide	NH_4OH	35.05	0.90	"	25.5			Ammonia water
			0.97	"	7.09			

. **Developing Agents**

Name	Formula	Molecular Weight	Solubility	Common Name
Paradihydroxymonochlorbenzene or Paradihydroxymonobrombenzene	$C_6H_3 (OH)_2 Cl$ or $C_6H_3 (OH)_2 Br$	128.50 172.96	Fairly soluble Fairly soluble	Adurol
Paradiamidophenol hydrochloride	$C_6H_3 (OH) (NH_2HCl)_2$	197.02		Amidol
Benzylparamidophenol	$C_6H_4 (OH) (NHCH_2C_6H_5)$	199.114	Fairly soluble	Duratol
Amidohydroxybenzyl alcoho	$C_6H_3 (OH) (CH_2OH) (NH_2)$	139.082	8 g. per 100 g. water	Edinol
$\alpha_1$amido-β_1 naphthol-β_3 sulphonic ac	$C_{10}H_5 (OH) (NH_2) (SO_3Na)$	261.144	Sparingly soluble, readily with alkali	Eikonogen
Parahydroxyphenylglycine	$C_6H_4 (OH) (NHCH_2COOH)$	167.082	Insoluble in water; soluble with alkali	Glycin
Paradihydroxybenzene	$C_6H_4 (OH)_2$, para	110.048	17 g. per 100 g. water	Hydrochinon
Monomethylorthoamidopheno sulphate	$2 [(C_6H_4) (OH) (NHCH_3)] (H_2SO_4)$	344.25	Easily soluble	Metol
Monomethylorthoamidopheno + Paradihydroxybenzene	$C_6H_4 (OH) (NHCH_3)$, ortho + $C_6H_4 (OH)_2$, para	233.13	Very soluble	Ortol
Orthodihydroxybenzene	$C_6H_4 (OH)_2$, ortho	110.048	8 g. per 100 g. water	Pyrocatechin
1, 2, 3, trihydroxybenzene	$C_6H_3 (OH)_3$, 1, 2, 3	126.048	Easily soluble	Pyrogallic acid
Monomethylparamidopheno + Paradihydroxybenzene	$C_6H_4 (OH) (NHCH_3)$, para + $C_6H_4 (OH)_2$, para	233.13	....	Quinomet
Paramidophenol hydrochloride	$C_6H_4 (OH) (NH_2HCl)$, para	145.534	....	Rodina

3. Inorganic Compounds

Name	Formula	Molecular Weight	Solubility in Grams per 100 g. Solution		Common Name
			Temp.	Weight	
Aluminum potassium sulphate	$KAl(SO_4)_2 \cdot 12H_2O$	472.532	15°C	9.59	Alum
Ammonium bromide	NH_4Br	97.962	20°	42.5	Ammonium bromide.
Ammonium carbonate	$HNH_4CO_3 \cdot NH_2NH_4CO_3$		15°	100. per 100. g. water	Ammonium carbonate
Ammonium chloride	NH_4Cl	53.502	15°	26.0	Sal ammoniac
Ammonium dichromate	$(NH_4)_2Cr_2O_7$	252.084	30°	32.05	Ammonium bichromate
Ammonium persulphate	$(NH_4)_2S_2O_8$	228.224	0°	58.2 per 100. g. water	Ammonium persulphate
Calcium carbonate	$CaCO_3$	100.13		Insoluble	Chalk
Calcium chloride	$CaCl_2$	111.05	20°	42.7	Calcium chloride
Calcium hypochlorite	CaO_2Cl		15°	0.25 per 100. g. water	Chloride of lime
Ceric sulphate	$Ce(SO_4)_2 \cdot 4H_2O$	404.454		Slightly sol. in water; sol. in sulphuric acid	Cerium persulphate
Chromium potassium sulphate	$KCr(SO_4)_2 \cdot 12H_2O$	499.432	25°	24.39 per 100 g. water	Chrome alum
Cupric sulphate	$CuSO_4 \cdot 5H_2O$	249.72	20°	17.2	Copper sulphate; blue vitriol
Ferric chloride	$FeCl_3 \cdot 6H_2O$	270.316	20°	47.88 (anhydrous salt)	Iron perchloride
Ferrous sulphate	$FeSO_4 \cdot 7H_2O$	278.022	25°	26.42 per 100. g. water (anhydrous)	Iron protosulphate; green vitriol
Gold trichloride (Auric chloride)	$AuCl_3 \cdot HCl \cdot 4H_2O$	412.112		68. per 100. g. water ($AuCl_3$)	Chloride of gold
Iodine	I_2	253.84	15°	0.272 to 0.283	Iodine
Magnesium	Mg	24.32		Insoluble	Magnesium
Mercuric chloride	$HgCl_2$	273.29	20°	5.4	Corrosive sublimate
Mercurous chloride	Hg_2Cl_2	473.66		Insoluble	Calomel
Mercuric iodide	HgI_2	327.29		Insoluble	Iodide of mercury
Potassium bromide	KBr	119.02	20°	39.5	Bromide of potash
Potassium carbonate	K_2CO_3	138.2	20°	52.8	Carbonate of potash

3. Inorganic Compounds—(*Concluded*)

Name	Formula	Molecular Weight	Solubility in Grams per 100 g. Solution		Common Name
			Temp.	Weight	
Potassium chlorate	$KClO_3$	122.56	20°	6.76	Chlorate of potash
Potassium chloride	KCl	74.56	20°	25.4	Chloride of potash
Potassium chloroplatinate	K_2PtCl_6	486.16	20°	1.12 per 100. g. water	Potassium chloroplatinate
Potassium chloroplatinite	K_2PtCl_4	413.24		Moderately soluble	Potassium chloroplatinite
Potassium dichromate	$K_2Cr_2O_7$	294.2	20°	12.	Bichromate of potash
Potassium disulphite	$K_2S_2O_5$	222.34		Slowly soluble	Potassium metabisulphite
Potassium hydroxide	KOH	56.108	20°	52.8	Caustic potash
Potassium iodide	KI	166.02	20°	59.0	Iodide of potash
Potassium permanganate	MnO_4	158.03	19.8°	5.96	Permanganate of potash
Silver nitrate	$AgNO_3$	169.89	20°	68.0	Nitrate of silver; lunar caustic
Sodium borate	$Na_2B_4O_7 \cdot 10H_2O$	382.16	21.5°	2.8 per 100. g. water	Borax
Sodium carbonate	Na_2CO_3	106.0	20°	17.7	Sal soda
Sodium chloride	$NaCl$	58.46	20°	26.37	Chloride of sodium
Sodium dichromate	$Na_2Cr_2O_7$	298.032	18°	63.92	Bichromate of soda
Sodium hydroxide	$NaOH$	40.008	20°	52.2	Caustic soda
Sodium hydrogen phosphate	$HNa_2PO_4 \cdot 12H_2O$	358.24	20°	9.3 (anhydrous)	Phosphate of soda
Sodium sulphide	$Na_2S \cdot 9H_2O$	240.214		Soluble	Sodium sulphide
Sodium sulphite	Na_2SO_3	126.07	20°	25.8 per 100. g. water	Sulphite of soda
Sodium thiosulphate	$Na_2S_2O_3 \cdot 5H_2O$	248.22	19.5°	171. xtls. per 100. g. of water	Hyposulphite of soda; "Hypo"
Uranyl nitrate	$UO_2(NO_3)_2 \cdot 6H_2O$	502.616	20°	200. xtls. per 100. g. of cold water	Uranium nitrate
Vanadic chloride	$2VO_2 \cdot 4HCl \cdot 3H_2O$	365.92		Very soluble	Vanadium chloride

Sodium disulfit

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4 Organic Compounds

Name	Formula	Molecular Weight	Solubility in Grams per 100 g. Solution		Common Name
			Temp.	Weight	
Acetone	$(CH_3)_2CO$	58.048		Sol. in all proportions	Acetone
Acetone sodium bisulphite	$(CH_3)_2C(OH)(SO_3Na)$	162.126		Readily soluble	Acetone sulphite
Ammonium sulphocyanide	NH_4SCN	76.122	20°	162.2 per 100. g. water	Ammonium sulphocyanate (thiocyanate)
Arrowroot starch	$(C_6H_{10}O_5)n$				Arrowroot
Ethyl alcohol	C_2H_5OH	46.048		Soluble in all proportions	Grain alcohol
Ethyl ether	$(C_2H_5)_2O$	74.08	20°	6.5	Ether; sulphuric ether
Ferric ammonium citrate	$5FeC_6H_5O_7\cdot 2(NH_4)_3C_6H_5O_7\cdot H_2NH_4C_6H_5O_7\cdot 2H_2O$			Soluble	Citrate of iron and ammonia
Ferric ammonium oxalate	$Fe(NH_4)_3(C_2O_4)_3\cdot 3H_2O$	428.014		4.7 per 100. g. water	Oxalate of iron and ammonia
Ferric oxalate	$Fe_2(C_2O_4)_3$	375.68		Soluble	Oxalate of iron
Ferric potassium oxalate	$FeK_2(C_2O_4)_3\cdot 3H_2O$	491.188		6. per 100. g. water	Oxalate of iron and potash
Formaldehyde	CH_2O	30.016		Contains about 40%	Formalin
Gelatine					Gelatine
Gylcerine	$C_2H_5(OH)_3$	92.064		Sol. in all proportions	Glycerine; glycero
Gum arabic					Gum arabic
Lead acetate	$Pb(C_2H_3O_2)_2\cdot 3H_2O$	379.196	25°	50. [$Pb(C_2H_3O_2)_2$]	Sugar of lead
Methyl alcohol	CH_3OH	32.032		Sol. in all proportions	Wood alcohol
Potassium citrate	$K_3C_6H_5O_7\cdot H_2O$	324.356	31.25°	169.7 (anhydrous) per 100. g. water	Citrate of potash
Potassium ferricyanide	$K_3FeC_6N_6$	329.2	20°	43.0 per 100. g. water	Red prussiate of potash
Potassium ferrocyanide	$K_4FeC_6N_6\cdot 3H_2O$	422.348	20°	25. to 40. per 100. g. water	Yellow prussiate of potash
Potassium oxalate	$K_2C_2O_4\cdot H_2O$	184.216	25°	27.4 (anhydrous)	Oxalate of potash
Potassium sodium tartrate	$KNaC_4H_4O_6\cdot 4H_2O$	282.196			
Sodium acetate	$NaC_2H_3O_2\cdot 3H_2O$	136.072	20°	32.9	Acetate of soda
Sodium citrate	$2Na_3C_6H_5O_7\cdot 11H_2O$	668.336	25°	90.9 per 100. g. water	Citrate of soda

Appendix

TABLE I

THE CHEMICAL ELEMENTS AND THEIR ATOMIC WEIGHTS (1915)

Elements		At. Wts.	Elements		At. Wts.	Elements		At. Wts.
Aluminum	Al	27.1	Holmium	Ho	163.5	Rhodium	Rh	102.9
Antimony	Sb	120.2	Hydrogen	H	1.008	Rubidium	Rb	85.45
Argon	A	39.88	Indium	In	114.8	Ruthenium	Ru	101.7
Arsenic	As	79.96	Iodine	I	126.92	Samarium	Sa	150.4
Barium	Ba	137.37	Iridium	Ir	193.1	Scandium	Sc	44.1
Bismuth	Bi	208.0	Iron	Fe	55.84	Selenium	Se	79.2
Boron	B	11.0	Krypton	Kr	82.92	Silicon	Si	28.3
Bromine	Br	79.92	Lanthanum	La	139.0	Silver	Ag	107.88
Cadmium	Cd	112.40	Lead	Pb	207.10	Sodium	Na	23.00
Caesium	Cs	132.81	Lithium	Li	6.94	Strontium	Sr	87.63
Calcium	Ca	40.17	Lutesium	Lu	174.0	Sulphur	S	32.07
Carbon	C	12.00	Magnesium	Mg	24.32	Tantalum	Ta	181.5
Cerium	Ce	140.25	Manganese	Mn	54.93	Tellurium	Te	127.5
Chlorine	Cl	35.46	Mercury	Hg	200.6	Terbium	Tb	159.2
Chromium	Cr	52.0	Molybdenum	Mo	96.0	Thallium	Tl	204.0
Cobalt	Co	58.97	Neodymium	Nd	144.3	Thorium	Th	232.4
Columbium	Cb	93.5	Neon	Ne	20.2	Thulium	Tm	168.5
Copper	Cu	63.57	Nickel	Ni	58.68	Tin	Sn	119.0
Dysprosium	Dy	162.5	Niton	Nt	222.4	Titanium	Ti	48.1
Erbium	Er	167.7	Nitrogen	N	14.01	Tungsten	W	184.0
Europium	Eu	152.0	Osmium	Os	190.9	Uranium	U	238.5
Fluorine	F	19.0	Oxygen	O	16.00	Vanadium	V	51.0
Gadolinium	Gd	157.3	Palladium	Pd	106.7	Xenon	Xe	130.2
Gallium	Ga	69.9	Phosphorus	P	31.04	Ytterbium	Yb	172.0
Germanium	Ge	72.5	Platinum	Pt	195.2	Yttrium	Yt	89.0
Glucinum	Gl	9.1	Potassium	K	39.10	Zinc	Zn	65.37
Gold	Au	197.2	Praseodymium	Pr	140.6	Zirconium	Zr	90.6
Helium	He	3.99	Radium	Ra	226.4			

TABLE II

METRIC MEASURES AND THEIR EQUIVALENTS

Standards

The metric standard unit of length is the meter, one ten-millionth part of the (assumed) length of the quadrant of a terrestrial meridian.

The metric standard unit of weight is the weight of one liter (1,000 cubic centimeters) of pure water at its greatest density (+ 4° C and 760 millimeters pressure) and is called the kilogram, or kilo.

Measures of Length

Millimeters	Centimeters	Decimeters	Meters	Inches	Feet	Yards
1.0	0.1	0.01	0.001	0.03937	0.00328	0.00109
10.0	1.0	0.10	0.010	0.39371	0.03281	0.01094
100.0	10.0	1.00	0.100	3.93708	0.32809	0.10936
1000.0	100.0	10.00	1.000	39.37079	3.28091	1.09363

1 inch = 2.5399 cm.
1 foot = 3.0479 dm.

1 yard = 0.9144 m.
1 mile = 1.6093 km. (Kilometer)

Measures of Volume

Cubic centimeters	Liters, or cubic decimeters	Cubic inches	Cubic feet	Drams	Ounces	Pints
1.0	0.001	0.06103	0.000035	0.270	0.034	0.002
10.0	0.010	0.61027	0.000353	2.71	0.338	0.021
100.0	0.100	6.10271	0.003532	27.05	3.381	0.211
1000.0	1.000	61.02705	0.035317	270.46	33.81	2.113

1 dram = 3.697 cc.
1 ounce = 29.572 cc.
1 pint = 473.152 cc.

1 cu. in. = 16.3862 cc.
1 cu. ft. = 28.3153 l.
1 cu. yd. = 764.5134 l.

Measures of Weight

Milligrams	Cg.	Dg.	Grams	Kilograms	Grains	Troy Ounces	Avoird. Ounces	Avoird. Pounds
1.0	0.1	0.01	0.001	0.000001	0.0154	0.000032	0.000035	0.00000
10.0	1.0	0.10	0.010	0.000010	0.1543	0.000322	0.000353	0.00002
100.0	10.0	1.00	0.100	0.000100	1.5432	0.003215	0.003527	0.00022
1000.0	100.0	10.00	1.000	0.001000	15.4323	0.032151	0.035274	0.00220
			10.000	0.010000	154.3235	0.32151	0.35274	0.02205
			100.000	0.100000	1543.2349	3.2151	3.5274	0.22046
			1000.000	1.000000	15432.3488	32.151	35.274	2.2046

1 grain = 0.06479895 g.
1 troy oz. = 31.103496 g.
1 av. oz. = 28.34954 g.

1 avoir. lb. = 0.45359265 kg.
1 avoir. lb. = 453.59265 g.
1 cwt. = 50.80237689 kg.

Abbreviations

Millimeter = mm.
Centimeter = cm.
Decimeter = dm.
Meter = m.

Cu. centim. = cc.
Liter = l.
Milligram = mg.
Centigram = cg.

Decigram = dg.
Gram = g.
Kilogram = kg.

TABLE III

POISONS AND THEIR ANTIDOTES

Adapted from "Facts, Figures, and Formulas o Photography"

Acids

Poison	Identification	Antidotes
Acetic	Smell	Chalk; plaster from the wall, plenty of water
Carbolic	Smell	*Zinc sulphate (1.5 gram) as emetic; warm water
Hydrochloric	Reddens litmus; ppts. white silver chloride in silver nitrate solution.	Chalk; plaster from the wall; large doses of water
Nitric	Reddens litmus; brown fumes when heated	Ditto
Oxalic	Ppts. white calcium oxalate with calcium chloride	*Zinc sulphate as emetic; then chalk or plaster, and water
Pyrogallic	Turns brown when shaken in alkaline solution	*Zinc sulphate as emetic
Sulphuric	Moistened paper chars when gently heated. Ppts. white in barium chloride solution	Chalk, or plaster, and then very large doses of water

Alkalies

Poison	Identification	Antidotes
Ammonium carbonate	Smell	Large quantities of water; then vinegar and water
Ammonium hydroxide	Smell	Ditto
Potassium carbonate	Turns litmus blue	Ditto
Potassium hydroxide	Ditto	Ditto
Sodium carbonate	Ditto	Ditto
Sodium hydroxide	Ditto	Ditto

Inorganic Substances

Poison	Identification	Antidotes
Antimony compounds	Ppts. white when acid solution is abundantly diluted; orange with very little sodium sulphide	*Emetic (antimony itself may act as emetic) followed by dose of strong tea
Arsenic compounds	Have chemical analysis made	*Emetic of zinc sulphate. Afterwards add a little diluted sodium hydroxide to solution of ferrous sulphate and administer the whole
Copper compounds	Appearance; blue soln. with ammonium hydroxide	White of egg and plenty of water
Gold compounds	Appearance	*Emetic of zinc sulphate
Iodine	Appearance and smell	*Emetic of zinc sulphate followed by boiled rice

POISONS AND THEIR ANTIDOTES—(*concluded*)

Inorganic substances—(*concluded*)

Poison	Identification	Antidotes
Lead compounds	Ppts. white with hydrochloric acid; ppt. dissolves when heated	*Emetic of zinc sulphate; followed by 15 grams of magnesium sulphate
Mercury compounds	Ppts. white with ammonium hydroxide; yellow with sodium or potassium hydroxide	*Emetic of zinc sulphate
Platinum compounds	Appearance	Ditto
Potassium dichromate	Ditto	*Emetic of zinc sulphate, followed by chalk, and water afterwards
Silver nitrate	Ppts. white with hydrochloric acid; ppt. dissolves in ammonium hydroxide	Plenty of common salt and warm water
Uranium compounds	Yellow appearance	*Emetic of zinc sulphate
Zinc chloride	Turns litmus red. Ppts. white with sodium hydroxide; ppt. dissolves in excess of alkali	Chalk, or plaster, and plenty of warm water

Organic Substances

Poison	Identification	Antidotes
Chloroform	Smell	Fresh air and artificial respiration
Ether	Smell	Ditto
Petroleum and mineral oils, including benzene, turpentine, etc.	Smell	*Emetic of zinc sulphate
Potassium cyanide	Odor of almonds. Dissolves silver	No certain remedy. 0.2 gram is a fatal dose. *Emetic of zinc sulphate; followed by solution of ferrous sulphate made slightly alkaline with weak sodium hydroxide. Artificial respiration

N.B.—Potassium ferricyanide, ferrocyanide and sulphocyanide are not poisonous in the ordinary sense.

Potassium oxalate	Ppts. white calcium oxalate with calcium chloride	*Emetic of zinc sulphate
Potassium dichromate and certain of the organic reducing agents, such as metol, duratol, etc., produce unpleasant and slow-healing skin affections upon some persons.		Remedy. If serious, abandon entirely the use of the cause of irritation. Keep hands out of the solutions; use rubber gloves; wash hands with carbolic soap

*NOTE.—When zinc sulphate is given as the antidote, 1.5 gram, dissolved in water, is always meant. If zinc sulphate is not to be had, mustard and warm water will serve the purpose.

TABLE IV

DEVELOPER FORMULAS

Adurol

Adurol	0.07	G.-M.S.	Take	23.3	cc.	3.0 N sodium sulphite
Sodium sulphite	0.70	N		25.3	cc.	3.0 N potassium carbonate
Potassium carbonate	0.76	N		0.9	g.	dry Adurol, dissolve, and dilute to 100 cc

Keeps extremely well.

Amidol

1. Normal developer

Amidol	0.025	G.-M.S.	Take	31.0	cc.	3.0 N sodium sulphite
Sodium sulphite	0.93	N		0.5	g.	dry Amidol, dissolve, and dilute to 100 cc.

2. For rapid exposures

Amidol	0.025	G.-M.S.	Take	20.7	cc.	3.0 N sodium sulphite
Sodium sulphite	0.62	N		0.5	g.	dry Amidol
Potassium bromide	0.008	N		0.8	cc.	1.0 N potassium bromide, and dilute to 100 cc.

Duratol

Duratol	0.004	G.-M.S.	Take	13.0	cc.	3.0 N sodium sulphite
Hydrochinon	0.037	G.-M.S.		30.0	cc.	3.0 N sodium carbonate
Potassium disulphite	0.037	N		0.2	g.	potassium disulphite
Sodium sulphite	0.38	N		0.1	g.	dry Duratol
Sodium carbonate	0.90	N		0.5	g.	dry Hydrochinon, and dissolve according to directions

A. Dissolve the potassium disulphite, Duratol, and Hydrochinon in 30 or 40 cc. of water and dilute to 50 cc.
B. Mix the 3.0 N sulphite and carbonate solutions and dilute the mixture to 50 cc.
Pour A into B, with stirring. No precipitation will occur if the developer be mixed in this manner.

Edinol

Edinol	0.036	G.-M.S.	Take	26.3	cc.	3.0 N sodium sulphite
Sodium sulphite	0.79	N		0.5	g.	dry Edinol; when dissolved add
Sodium carbonate	0.96	N		32.0	cc.	3.0 N sodium carbonate, and dilute to 100 cc.

This developer is particularly suitable for bromide and gaslight papers, and for transparencies.

DEVELOPER FORMULAS—(*continued*)

Eikonogen					
Eikonogen	0.019	G.-M.S.	Take	26.3 cc.	3.0 N sodium sulphite
Sodium sulphite	0.79	N		23.7 cc.	3.0 N sodium carbonate
Sodium carbonate	0.71	N		0.5 g.	dry Eikonogen, and dilute to 100 cc.
Good for short exposures.					
Glycin					
1. Glycin	0.167	G.-M.S.	Take	23.3 cc.	3.0 N sodium sulphite
Sodium sulphite	0.70	N		43.3 cc.	3.0 N potassium carbonate
Potassium carbonate	1.30	N		1.8 g.	dry Glycin, and dilute the solution to 100 cc
2. For tank development					
Glycin	0.013	G.-M.S.	Take	58.0 cc.	3.0 N sodium sulphite
Sodium sulphite	0.786	N		69.0 cc.	3.0 N potassium carbonate
Potassium carbonate	0.174	N		0.4 cc.	1.0 N potassium bromide
Potassium bromide	0.0004	N		2.2 g.	dry Glycin, and dilute to 1000 cc.
Hydrochinon					
Hydrochinon	0.045	G.-M.S.	Take	10.7 cc.	3.0 N sodium sulphite
Sodium sulphite	0.32	N		31.7 cc.	3.0 N sodium carbonate
Sodium carbonate	0.95	N		0.5 g.	dry Hydrochinon, and dilute to 100 cc.
Metol-Hydrochinon					
1. For average negatives					
Metol	0.0073	G.-M.S.	Take	29.0 cc.	3.0 N sodium sulphite
Hydrochinon	0.023	G.-M.S.		39.7 cc.	3.0 N potassium carbonate
Sodium sulphite	0.87	N		5.0 cc.	1.0 N potassium bromide
Potassium carbonate	1.19	N		0.25 g.	dry Metol
Potassium bromide	0.05	N		0.25 g.	dry Hydrochinon. Dissolve the Metol in 6-8 cc. of water, add the other solutions; add the Hydrochinon, and make up to 100 cc.
2. For bromide paper					
Metol	0.017	G.-M.S.	Take	29.0 cc.	3.0 N sodium sulphite
Hydrochinon	0.027	G.-M.S.		34.7 cc.	3.0 N sodium carbonate
Sodium sulphite	0.87	N		10.0 cc.	1.0 N potassium bromide
Sodium carbonate	1.04	N		0.6 g.	dry Metol
Potassium bromide	0.10	N		0.3 g.	dry Hydrochinon, and dilute to 100 cc. (See No. 1 above)

DEVELOPER FORMULAS—(*concluded*)

3. For gaslight paper					
Metol	0.0064	G.-M.S.	Take	42.3 cc.	3.0 N sodium sulphite
Hydrochinon	0.054	G.-M.S.		50.3 cc.	3.0 N sodium carbonate
Sodium sulphite	1.27	N		0.7 cc.	1.0 N potassium bromide
Sodium carbonate	1.51	N		0.22 g.	dry Metol
Potassium bromide	0.007	N		0.6 g.	dry Hydrochinon, and dilute to 100 cc. (See No. 1 above)
Ortol			Take	58.3 cc.	3.0 N sodium sulphite
Ortol	0.038	G.-M.S.		35.3 cc.	3.0 N potassium carbonate
Sodium sulphite	1.75	N		0.4 cc.	1.0 N potassium bromide
Potassium carbonate	1.06	N		0.9 g.	dry Ortol
Potassium bromide	0.004	N		0.23 g.	potassium disulphite, and dilute to 100 cc.
Pyrogallic acid					
1. Wellington "Pyro-Soda"					
Pyrogallic acid	0.05	G.-M.S.	Take	17.0 cc.	3.0 N sodium sulphite
Sodium sulphite	0.50	N		12.0 cc.	3.0 N sodium carbonate
Citric acid	0.01	N		1.0 cc.	1.0 N citric acid
Sodium carbonate	0.35	N		0.6 g.	dry Pyrogallic acid, and dilute to 100 cc
2. Another formula					
Pyrogallic acid	0.071	G.-M.S.	Take	29.0 cc.	3.0 N sodium sulphite
Sodium sulphite	0.87	N		34.7 cc.	3.0 N sodium carbonate
Sodium carbonate	1.04	N		0.9 g.	dry Pyrogallic acid, and dilute to 100 cc.
Pyrocatechin					
1. A good, slow developer					
Pyrocatechin	0.061	G.-M.S	Take	7.0 cc.	3.0 N sodium sulphite
Sodium sulphite	0.21	N		42.0 cc.	3.0 N potassium carbonate
Potassium carbonate	1.26	N		0.67 g.	dry Pyrocatechin, and dilute to 100 cc.
2. For bromide paper					
Pyrocatechin	0.045	G.-M.S.	Take	6.7 cc.	3.0 N sodium sulphite
Sodium sulphite	0.20	N		15.7 cc.	3.0 N sodium carbonate
Sodium carbonate	0.47	N		0.5 g.	dry Pyrocatechin, and dilute to 100 cc.

Pyrocatechin developer is said to keep as long as two years.

TABLE V

FIXING BATH FORMULAS

Sodium thiosulphate, crystallized, $Na_2S_2O_3.5H_2O$; molecular weight, 248.22; percentage of $Na_2S_2O_3$ in the crystallized salt, 63.709%.

For reduction purposes, where the thiosulphate is oxidized, as by iodine, to tetrathionate, a 1.0 N solution contains 248.22 grams of the crystallized salt per liter of solution.

For the reaction of metathesis whereby soluble silver-sodium thiosulphate is formed, a 1.0 N solution contains 248.22 grams of the crystallized salt per liter of solution.

1. An average formula for plates; also for lanternslides
   Make an approximately 0.8 N thiosulphate solution:

Sodium thiosulphate..................	200.	grams
Water, to	1000.	cc.

2. For films; also for plates
   Make an approximately 1.0 N thiosulphate solution:

Sodium thiosulphate	250.	grams
Water, to..........................	1000.	cc.

Leave plates and films in the solution until all creaminess has disappeared, and then for as long again. The whole time will ordinarily be about 20 minutes.

3. For bromide and gaslight papers
   A 0.8 N thiosulphate solution:

Sodium thiosulphate..................	200.	grams
Water, to..........................	1000.	cc.

Prints will be fixed in 10 to 15 minutes.

4. For printing-out papers
   A 0.4 N thiosulphate solution:

Sodium thiosulphate..................	100.	grams
Water, to..........................	1000.	cc.

Soak prints for at least 10 minutes.

N.B.—These plain thiosulphate solutions are to be used at a temperature of about + 18°C (65°F); and must be made up fresh

FIXING BATH FORMULAS—*(continued)*

5. Acid fixing-bath, for plates, films, and developing-out papers.

An 0.8 N thiosulphate solution, containing potassium disulphite (metabisulphite):

Sodium thiosulphate	200.	grams
Potassium disulphite	25.	grams
Water, to	1000.	cc.

6. For fixing the bleached print in the bromoil process:

Approximately 0.4 N thiosulphate:

Sodium thiosulphate	48.	grams
Sodium sulphite	24.	grams
Water, to	500.	cc.

Leave the print in this bath 2 or 3 minutes.

7. Hardening bath, using formaldehyde.

Formaldehyde	50.	cc.
Water, to	500.	cc.

Give 5 minutes; or use ½ the above concentration and soak plates or films for 15 minutes.

8. Hardening bath, with chrome alum.

Potassium chromium sulphate	15.	grams
Water, to	500.	cc.

Immerse for 10 to 15 minutes.

N.B.—Ordinary alum, potassium aluminum sulphate, should not be used for hardening purposes, since the results are not so permanent as with formaldehyde or chrome alum.

It is much better practice to keep the hardening solution separate from the acid fixing bath.

9. Acid fixing and hardening bath, for negatives and developing-out papers.

Sodium thiosulphate (0.9 N)	220.	grams
Potassium disulphite	28.	grams
Potassium chromium sulphate	28.	grams
Water, to	1000.	cc.

10 Cramer's acid fixing and hardening bath.

A.	Potassium chromium sulphate	15.	grams
	Potassium disulphite	22.5	grams
	Water, to	250.	cc.
B.	Sodium thiosulphate (1.0 N)	250.	grams
	Water, to	1000.	cc.

When solution and filtration have been effected, pour A into B with constant stirring.

FIXING BATH FORMULAS—(*concluded*)

11. To test a fixing bath for exhaustion:

Place a drop of the solution on white paper; expose it to light and air. If it turns brown, the solution is worked out.

TABLE VI

FORMULAS FOR INTENSIFICATION

1. Wellington Silver Intensifier.

No. 1

Ammonium sulphocyanide	40. grams
Sodium thiosulphate	40. grams
Water, to	250. cc.

No. 2

Silver nitrate	25. grams
Water, to	250. cc.

No. 3

Sodium sulphite	2.0 grams
Pyrogallic acid	1.0 grams
Water, to	10. cc.

No. 4

Ammonium hydroxide (conc.)	10. cc.
Water, to	100. cc.

For use, add 15 cc. No. 2 to the same volume of No. 1 with stirring. Enough of No. 1 is then to be added just to dissolve the precipitated silver sulphocyanide, and no more. To this mixture add 2 cc. each of No. 3 and No. 4 solutions. Put the dry negative into this bath. Intensification will take place in from 5 to 20 minutes. Greater rapidity and more density can be secured by the addition of more of No. 4.

2. Uranium Intensifier.

No. 1

Uranium nitrate	1. gram
Water, to	100. cc.

No. 2

Potassium ferricyanide	1. gram
Acetic acid (Glacial)	18. cc.
Water, to	100. cc.

FORMULAS FOR INTENSIFICATION—(*continued*)

Mix equal volumes of No. 1 and No. 2. After intensification has reached the desired point, wash for 10 minutes in running water.

3. Chromium Intensifier.

No. 1

Potassium dichromate	5.5	grams
Water, to	100.	cc.

No. 2

Hydrochloric acid (conc.)	5.5	cc.
Water, to	100.	cc.

Mix 1 volume of No. 1, 1 volume of No. 2, and 2 volumes of water, just before using, as the mixture does not keep well. Bleach the negative completely, wash out the chromic acid, expose to daylight, and re-develop in a developing solution suited to bromide paper.

4. Mercury Intensifiers.

Negatives must be well washed after fixing and before intensification.

A. Mercuric chloride.

Mercuric chloride	2.	grams
Water, to	100.	cc.

B. Mercuric bromide

Mercuric chloride	2.	grams
Potassium bromide	2.	grams
Water, to	100.	cc.

Bleach the negative thoroughly in either of the above solutions; wash for 10 to 15 minutes, and develop the white image in daylight either in sodium thiosulphate solution (1 in 10), or in amidol developer. Wash and dry.

FORMULAS FOR INTENSIFICATION—*(concluded)*

C. Mercuric iodide.

Negatives do not need a careful washing before intensification by this method.

Mercuric chloride	2.	grams
Potassium iodide	2.	grams
Sodium sulphite	20.	grams
Water, to	100.	cc.

The negative is intensified directly in this bath, but must be subsequently treated with a developer to prevent fading.

TABLE VII

FORMULAS FOR REDUCTION

1. For uniform reduction, as of over-developed negatives.
Permanganate Reducer

Potassium permanganate	0.5	gram
Sulphuric acid (conc.)	2.	cc.
Water, to	200.	cc.

Dissolve the permanganate in, say, half of the water, add the sulphuric acid to this solution, and dilute to the volume specified.

For use, dilute 1 volume of the stock solution up to 4 volumes with water. When the density has been enough diminished, rinse the plate and put it for 5 minutes in an acid thiosulphate fixing bath. Wash well.

2. For reducing shadow details, *i.e.*, increasing contrast, as in over-exposed negatives.
Farmer's Ferricyanide Reducer

No. 1

Potassium ferricyanide	5.	grams
Water, to	50.	cc.

No. 2

Sodium thiosulphate	100.	grams
Water, to	1000.	cc.

Since ferricyanide does not keep well in solution, it is to be made up only as needed.

FORMULAS FOR REDUCTION—(*concluded*)

To 100 cc. of No. 2 add 5 to 10 cc. of No 1, immerse the plate, and rock the tray until the negative has been sufficiently reduced. Wash well.

3. For reduction of highlights, *i.e.*, to diminish contrast.

A. Ceric Sulphate Reducer

Ceric sulphate (crystals)	10. grams
Sulphuric acid (conc.)	4. cc.
Water, to	100. cc.

Take 1 volume of the stock solution and dilute with 1 volume of water. Rock the tray.

B. Bennett's Ammonium Persulphate Reducer

Ammonium persulphate	12. grams
Sodium sulphite	2. grams
Sulphuric acid (conc.)	1. cc.
Water, to	100. cc.

Dilute 1 volume of the stock solution with 4 to 8 volumes of water. After reduction, rinse the plate and put it for 6 minutes in an acid thiosulphate solution. Wash well.

4. For making bright bromide prints from weak negatives.

Wellington Iodide Reducer

Potassium iodide	2.0 grams
Iodine	0.2 grams
Water, to	300. cc.

After the bromide print, which must be somewhat over-developed, has been fixed and washed, it is put in the above bath and left until sufficiently lightened. Then put it in fresh thiosulphate solution for a few minutes and wash it thoroughly. In the iodide solution the whites of the print turn a dark blue owing to the formation of the iodide of starch with the sizing of the paper. This blue compound is destroyed again by the thiosulphate.

TABLE VIII

FORMULAS FOR DYEING PLATES FOR COLOR CORRECTION

Prepare stock solutions of dyes, by dissolving 1. gram of each in 95% ethyl alcohol and diluting with the same to 1,000 cc.

No. 1.	Acridine orange No. 0	For blue-green and green
No. 2.	Erythrosine	For greenish-yellow and yellow
No. 3.	Orthochrome T	For blue-green, green, and yellow
No. 4.	Pinaverdol	For green, yellow, and orange
No. 5.	Pinacyanol	For red-sensitiveness; to the extreme visible red. Gives very fast plates
No. 6.	Pinachrome	Sensitizes to line B. Plates are faster than with No. 3
No. 7.	Homocol	For red-sensitiveness
No. 8.	Dicyanine	For infra-red

Use Distilled Water

Blue-green Green	Greenish-yellow Yellow	Green, yellow Orange	Red*	Panchromatic† Effects
No. 1 200 cc.	No. 2 200 cc.	No. 3 2 cc.	No. 6 2 cc.	No. 4 11 cc.
Dil. to 1 l.	NH$_4$OH 10 cc.	Dil. to 1 l.	Dil. to 1 l.	No. 5 14 cc.
	Dil. to 1 l.	No. 4 2 cc.	Infra-red‡	No. 7 11 cc.
		Dil. to 1 l.	No. 8 2 cc.	NH$_4$OH 33 cc.
			Dil. 1 l.	
				Alcohol 400 cc.
			Red*	Dil. to 1 l.
			No. 7 2 cc.	
			Dil. to 1 l.	

*Sensitize without light.

†Use plates that are not too fast; sensitize without light.

‡Make up just before using, since the sensitizing power of the solution quickly diminishes.

When sensitizing, put the plates in a grooved trough or tank containing the dye. A tray can be used, if it is rocked constantly. Bathe the plates for 3 minutes; wash in running water for 3 minutes; and put to dry in a light-proof drying cupboard, or in a tight box with fused calcium chloride as a dehydrating agent.

TABLE IX

LIST OF APPARATUS FOR EXPERIMENTS

1	Alcohol lamp, or if available a Bunsen's burner with rubber connecting tube
1	Balance, capacity 100. grams to 0.05 gram
3	Beakers, glass, lipped, 100. cc. capacity
3	Beakers, glass, lipped, 250. cc. capacity
3	Beakers, glass, lipped, 500. cc. capacity
1	Cylinder, graduated, 10. cc. capacity
1	Cylinder, graduated, 50. cc. capacity
1	Cylinder, graduated, 250. cc. capacity
2	Dishes, porcelain evaporating, No. 0, 7.5 cm. diameter
1	Filter paper, package of 100 sheets, 18.5 cm. diameter
2	Flasks, glass, conical, 125. cc. capacity
1	Funnel, glass, 10. cm. diameter
1	Litmus paper, tube of 100 strips, red
1	Litmus paper, tube of 100 strips, blue
1	Mortar and pestle, porcelain, 15. cm. diameter
6	Stirring-rods, glass, 15. cm. length
12	Test tubes, glass, 15. cm. x 2. cm.
1	Weights, set, in block, 50. gram piece to 0.05 gram

TABLE X

LIST OF CHEMICALS FOR EXPERIMENTS

N.B.—No amounts are suggested for those chemicals which are commonly found on the photographer's shelves.

	Quantity	
Acetic acid, glacial, (Sp. Gr. 1.058), C.P.		
Ammonium hydroxide, conc., (Sp. Gr. 0.90), C.P.		
Citric acid, C.P.	50.	grams
Ethyl alcohol, 95%		
Ferric ammonium citrate, C.P.	50.	"
Ferric oxalate, C.P.	50.	"
Ferrous sulphate, cryst., C.P.	50.	"
Gelatine, photographic	500.	"
Hydrochloric acid, conc., (Sp. Gr. 1.20), C.P.		

LIST OF CHEMICALS FOR EXPERIMENTS *(concluded)*

Magnesium, powder (from box of flashlight)		
Mercuric chloride, C.P.	50.	grams
Nitric acid, conc., (Sp. Gr. 1.42), C.P.		
Potassium aluminum sulphate, cryst. C.P.	50.	"
Potassium bromide, C.P.		
Potassium dichromate, C.P.	50.	"
Potassium ferricyanide, C.P.	50.	"
Potassium ferrocyanide, C.P.	50.	"
Potassium iodide, C.P.	25.	"
Potassium oxalate, C.P.	50.	"
Potassium permanganate, C.P.	50.	"
Pyrogallic acid		
Silver nitrate, C.P.	50.	"
Sodium carbonate, anhydrous, C.P.		
Sodium chloride, C.P.	50.	"
Sodium sulphide, cryst., C.P.	50.	"
Sodium sulphite, dry, C.P.		
Sodium thiosulphate, cryst., photographic		
Sulphuric acid, conc., (Sp. Gr. 1.84), C.P.		
Uranium nitrate, cryst., C.P.	25.	"

TABLE XI

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