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No 29.

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C. SORDES ELLIS, F.I.C., F.C.S.

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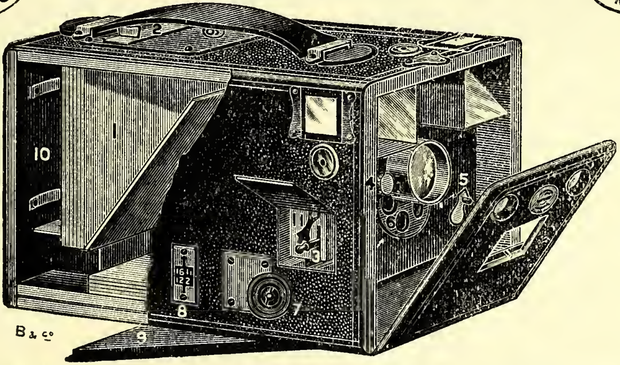

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THE ELEMENTARY CHEMISTRY
OF
PHOTOGRAPHIC CHEMICALS.

BY
C. SORDES ELLIS, F.I.C., F.C.S.

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THE ELEMENTARY CHEMISTRY
OF
PHOTOGRAPHIC CHEMICALS.

CHAPTER I.

INTRODUCTION.

Every one who dabbles in photography must take a greater or less interest in the properties, etc., of the chemicals used, and I trust that this book may lead to a few taking a more intelligent interest in photography than they have hitherto done.

The actual difference in composition between sodium sulphite, hypo, and Glauber's salts is very small. The two former are almost indispensable photographic reagents, whereas the third is at present almost useless, from our point of view. Again, the difference between sodium carbonate and bicarbonate is small, yet their actions differ so much, that the former is of the greatest use in photography, and the latter worse than useless if mistaken for the former. With a little knowledge of their chemistry, however, the useless can easily be turned into the useful. These and other such instances will be explained in the course of the following chapters.

Before I can proceed to intelligently explain the elementary chemistry of the most commonly used substances in photography, I shall have to give as short and concise a chapter as I possibly can on a few rudimentary principles underlying the science of chemistry. I hope thus to make my explanations equally clear to the persons who do not possess any knowledge of it, as to those who have a smattering of this most fascinating branch of science.

CHAPTER II.

GENERAL.

The chemical and physical properties of matter must not be confused. To make this difference clear, let me give two examples from near home. First, a good illustration of a physical change is seen in an ordinary limelight lantern. A new stick of lime is put in place, and a jet of burning hydrogen and oxygen is projected on a portion of it. The part on which the flame impinges gets hot and glows a very brilliant white. Now, when the source of heat is turned off, the lime gets cool again and is just the same as before the heating. It may crack certainly, but the only changes it has been through are physical ones. It was lime when cold, still lime when hot and glowing, and lime again when cold. Second, if allowed, however, to be exposed to *moist* air, a chemical change would take place; hence the necessity of keeping in air-tight tins. But, to illustrate changes in chemical properties, I will take another homely example. When taking a photo at night, or in a dark cellar or cave, a certain length of magnesium ribbon is burnt; during combustion a brilliant white light is emitted. The residue, however, is very different to the original ribbon, and if the ribbon were weighed and all the resulting fluffy powder collected, it would be found that the weight of the latter was one-half as heavy again as the former; hence there must have been a chemical change, a change in composition, the magnesium having combined with the oxygen of the atmosphere. Where you have a chemical change you have *ipso facto* a physical change; the converse of this, however, is not always true. By means of the above examples I have tried at some length to show the difference between the two sciences of physics and chemistry.

In order to elucidate what follows, I will now illustrate and define as many terms as I possibly can without actually giving definitions. Any further technical words or expressions that may be introduced will be explained as the occasion arises.

An *element* is a substance from which nothing but that substance can be obtained. Silver is an element. If a piece of pure silver be taken, no matter what treatment it is subjected to, nothing but silver can be obtained from it. If silver, however, could be split up into two substances, say A and N, then silver would no longer be an element, but a *compound* of the two elements, A and N. Up to the present this has not been done, hence my statement.

According to *Dalton's atomic theory*, every element is supposed to be divisible, and divisible until no further division can be imagined. This ultimate division is an *atom.* Please remember that this is theory, and no one ever expects to see the atoms, even if the strongest microscope was made thousands of times stronger. Every one of these small individual portions of an element always weighs exactly the same for the same element, but the weights of the atoms of various elements are all different. The absolute weight cannot, of course, be given, but if we take the lightest atom and call that one, then we know the *atomic weights* or relative weights of the others. Hydrogen, being the lightest, is taken as the unit, and the rest must be more than unity, as will be seen from the following table of elements occurring in compounds of photographic interest. The atomic weights are given to the nearest whole number; in Appendix I. the exact figures will be found.

NAME.	SYMBOL.	ATOMIC WEIGHT.
Hydrogen	H	1
Boron	B	11
Carbon	C	12
Nitrogen	N	14
Oxygen	O	16
Fluorine	F	19
Sodium	Na	23
Magnesium	Mg	24
Aluminium	Al	27

NAME.	SYMBOL.	ATOMIC WEIGHT.
Phosphorus	P	31
Sulphur	S	32
Chlorine	Cl	35·5
Potassium	K	39
Calcium	Ca	40
Cromium	Cr	52
Manganese	Mn	55
Iron	Fe	56
Copper	Cu	64
Bromine	Br	80
Silver	Ag	108
Antimony	Sb	120
Iodine	I	127
Cerium	Ce	140
Platinum	Pt	195
Gold	Au	197
Mercury	Hg	200
Lead	Pb	207
Uranium	U	239

When a chemist wishes to represent an element, instead of writing the name in full he writes its *symbol.* A list of those used in this book will be found above and one more complete in Appendix I. If fine iron filings be thoroughly mixed with powdered sulphur, we have a *mechanical mixture* ; a microscope will prove this ; the pieces of iron can be seen lying by the side of the pieces of sulphur. If, however, the mixture be heated, a *chemical change* takes place, and the resulting body would be ferrous sulphide, a *chemical compound* having different properties, etc., to either of its constituents. The reaction would be expressed by a *chemical equation* as follows:—

$$Fe + S = FeS,$$

and this would mean that one atom of sulphur had united with one of iron, forming a *molecule* of ferrous sulphide, and its *formula* would be FeS. One of the questions yet to be decided is—Does gelatine and silver haloid salts form a chemical compound or only a mechanical mixture?

A plus sign thus +, between two or more bodies or elements signifies a mechanical mixture, and no sign, or a bar, represents a chemical compound containing the elements represented in it and in the proportions of their atomic weights. Further, as the atoms have a definite weight relative to hydrogen, we can interpret more fully the above equation. Let us hypothesise and suppose, for the sake of explanation, that ten million atoms of hydrogen weigh a grain (which they do not), then ten million atoms of iron would weigh fifty-six grains, and the same number of sulphur atoms thirty-two grains, and ten million molecules of ferrous sulphide would weigh exactly $56 + 32 = 88$ grains. This reasoning can be applied to any chemical equation, no matter how complicated, and we shall find it of great use in calculating the various amounts of chemicals required to perform certain reactions and such like; in fact, I have no room here to simply enumerate the different calculations that could be made from these simple relations.

Crystallography is a most interesting, instructive, and fascinating study, especially with polarised light and a microscope fitted with a camera. Most substances crystallise by combining with water, which is known as *water of crystallisation.* For example, every molecule of sodium carbonate takes ten molecules of water when crystallising. It is represented thus—Na_2CO_3—$10H_2O$. This represents ordinary washing soda crystals which we see contain water. How much is soda and how much water? We will calculate the amount from the formula. A little figure underneath and after a symbol denotes that more than one atom of that element takes part in the reaction; and a large figure in front of a symbol multiplies the whole molecule or atoms following it by that number. To get the *molecular weight* of a body the number of atoms of each individual element is multiplied by their atomic weights and added together thus:—

$$
\begin{array}{lcr}
Na_2 & = 2 \times 23 = & 46 \\
C & = 1 \times 12 = & 12 \\
O_3 & = 3 \times 16 = & 48 \\
\hline
 & & 106 \\
\hline
\end{array}
$$

$$
\begin{array}{lcr}
10\ H_2 & = 20 \times \ \ 1 = & 20 \\
10\ O & = 10 \times 16 = & 160 \\
\hline
 & & 180 \\
\hline
\end{array}
$$

It will be seen that out of 286 (106 + 180) parts of soda crystals 180, or more than half of it, consists of water, which is given off on heating—but more of this in its proper place.

Crystals.—When a substance crystallises it does so in one of six ways, each of which is in a definite geometrical form.

NAME.	AXES.		EXAMPLES.
	POSITION.	NO.	
1. Regular or cubic	All equal and all at right angles	3	Diamond, common salt, alum, garnet, iron pyrites
2. Hexagonal	Three equal in one plane, cutting each other at 60°; one longer or shorter than the other three, but cutting their plane at right angles	4	Calc spar, ice, quartz
3. Quadratic	All at right angles; two equal, one longer or shorter than others	3	Potassium ferrocyanide, copper pyrites
4. Rhombic.	All at right angles, but all unequal	3	Zinc sulphate, heavy spar
5. Mono-symmetric or monoclinic.	All unequal; two at right angles, one inclined to plane of other two	3	Washing soda, borax, sodium phosphate, gypsum, ferrous sulphate, Glauber salts, hypo
6. Asymmetric or triclinic	All unequal; none at right angles	3	Potassium bichromate, copper sulphate

CHAPTER III.

SYSTEMS OF MEASUREMENT.

One could imagine a system of weights and measures more complicated and intricate than ours, but that is about the most that could be said in its favour. There is no simple relation between the different measures—*e.g.*, three barleycorns placed end to end are supposed to measure an inch, hence a barleycorn ought to be exactly a third of an inch in length. How far would this be accurate for a number of samples, say, to first decimal place? The answer is obvious. Again, an inch is the twelfth of a foot, and the latter a third of a yard. The same applies, and if anything in a more complicated degree, to the measures of volume and weight. In a word, a simple relation between the various measures does not exist. How many calculations the amateur or professional photographer would be saved if the makers of plates and papers would give their formulæ in the metric system, as is done in all scientific work, both in England and on the Continent! When a formula is given in parts it is much the same as giving it in the newer system; but many fail to appreciate its simplicity, because they are not familiar with it.

I will first discuss the measures of length, and show how the standard was obtained; then explain how the unit of volume is obtained from that of length; and, lastly, the weight from that of volume. Every one will at once be struck with the uniformity, not only between the different measures of the same kind, but between the whole three of length, volume, and weight.

BRITISH AND METRIC WEIGHTS AND MEASURES.

1. *Length.*—The Imperial Weights and Measures Act of 1824 legalised, and to a very large extent, simplified and reduced our system to something like order. The standard of length, as defined in the above Act, is the yard, and is the distance between two platinum points on a bronze bar at a temperature of 62° Fahrenheit (written F.), which is kept at the Exchequer Offices in London. The other measures of length are arbitrary, but not uniform, multiples or sub-multiples of this. In the metric system the standard of length is the metre, and was originally obtained in the following way:—Some French savants in 1799, after years of work, finally measured the quadrant of the earth from the Pole to the Equator; this distance, marked AB in fig. 1, was divided into ten million parts and one of these was called the

metre. With the advance in the manufacture of instruments of precision later researches have shown, however, that these original measurements were not quite exact, and the distance between the Pole and the Equator is not exactly ten million metres. The standard of length, as then arrived at, is, however, still retained as the unit.

For sub-multiples the metre was divided into ten equal parts each known as a decimetre, from *decima*—the Latin for tenth. Then the decimetre was again divided into ten parts, making a hundredth of a metre, and called centimetre, and so on. All the sub-multiples have the Latin prefix for the number by which they are divided, the corresponding Greek prefix denoting the multiples. The distance A B in fig. 2 equals five centimetres, or 0·5 (that is, a half) of a decimetre. The centimetre is still further

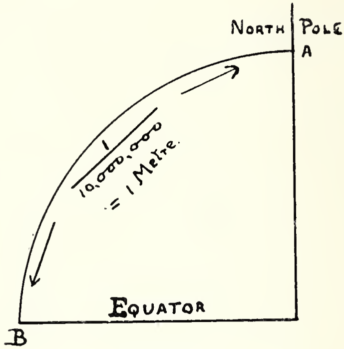


FIG. 1.

divided into another ten parts, each known as a millimetre (mille = 1,000). Of the multiples I will only mention here the kilometre, or the 1,000 metres, which is the long distance unit, corresponding to our mile.

For scientific and photographic purposes, the unit of length generally adopted is the centimetre, and not the metre.

1000 metres = 1 kilometre.
100 ,, = 1 hectometre.
10 ,, = 1 decametre.
·1 of a metre = 1 decimetre.
·01 ,, = 1 centimetre.
·001 ,, = 1 millimetre.

The British measures of length are too well known to be given here; a few approximate relations between the two systems may, however, help the reader to appreciate the above lengths.

1 foot = ·302 metres.
5 miles = 8 kilometres.
1 metre = 39·37 inches.
1 decimetre = 4 inches (nearly).

2. *Capacity.*—We have a standard of volume, whether it is the pint, quart, or gallon does not much matter; but in the metric system the unit is easily obtained from that of length. The capacity occupied by a cube built on an edge one decimetre long is taken as the basis of all measures of volume, and is called a litre. The cube shown in fig. 2 is exactly an eighth of a litre, AB = AC = CE, etc.

= ·5 of a decimetre, the cube of ·5 = ·125 = 1-8th; that is, eight cubes similar to A B C D E F G would form a cube of double the edge, or decimetre. The multiples and sub-multiples are the same as for length, and it is needless to repeat them all here. For all scientific purposes the cubic centimetre (written c.c.) is the generally accepted and most convenient unit. A cubic centimetre is sometimes, but rarely, called a millilitre.

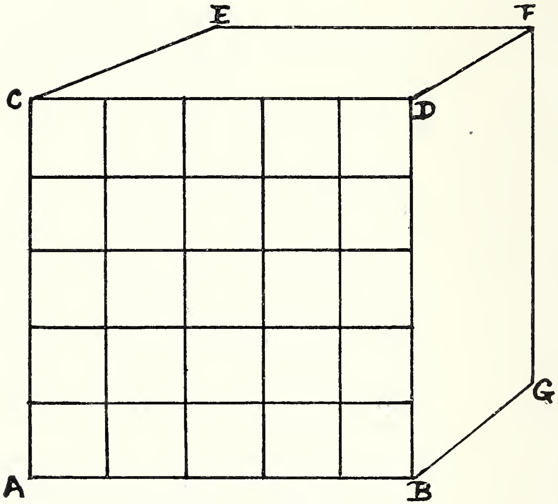


FIG. 2.

1,000 c.c. = 1 litre.
100 c.c. = 1 decilitre.
10 c.c. = 1 centilitre.
1 c.c. = 1 millilitre.

The British measures of volume being somewhat involved I append Apothecaries' (fluid) Measure, as used in photography.

60 minims = 1 fluid drachm (fl. dr.).
8 drachms = 1 ,, ounce (fl. oz.).
20 ounces = 1 pint.

The following relationships are interesting :—

1 litre = 61 cubic inches = 1·76 pints.
1 fluid ounce = 28·4 c.c.

3. *Weight.*—The British standard of weight, the pound avoirdupois, is the mass of a piece of platinum kept at the Exchequer along with the other standards. The metric unit is obtained by filling with distilled water a vessel which holds precisely one cubic centimetre, the exact size of which is shown in fig. 3 (AB in fig. 3 is exactly one-fifth of AB in fig. 2). The water, when the experiment is made, must be at the temperature of its maximum density—*i.e.*, 4° Centigrade. The mass or weight of this water is called a gramme. The multiples are the same as previously shown.

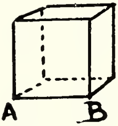


FIG. 3.

1,000 grammes = 1 kilogramme.
100 ,, = 1 hectogramme.
10 ,, = 1 decagramme.
·1 of a gramme = 1 decigramme.
·01 ,, = 1 centigramme.
·001 ,, = 1 milligramme.

Avoirdupois weights, as far as used in photography, I give below.

437·5 grains = 16 drams = 1 ounce.
16 ounces = 1 lb. = 7,000 grains.

The relationship between the two systems is complicated, but here are a few examples worth remembering:

A kilogramme, the unit by which hypo and such like are bought in France = 2·2 lb.
1 lb. (Avoir.) = 454 grammes approx. 1 gramme = 15·43 grains.
1 minim = ·05 c.c. approx.
1 fluid ounce of water weighs 1 ounce (Avoir.).
1 dram (Avoir.) is *not* the same as drachm (Ap.).
1 ounce ,, is the same as ounce (Ap.).
1 pound ,, ,, ,, pound (Ap.).

A list of factors for converting from one system to the other will be found in Appendix VII.

Measurements of Temperature.

When dealing with temperatures in scientific work the Centigrade scale is generally used (*Abbreviations*: C. = Centigrade; F. = Fahrenheit). In this system we have the freezing or melting point of water, marked 0 (32 in F. scale), and that of boiling water, 100 (212 in F.). The interval between these points is divided into a hundred parts, each of which is called a degree—C. This division into a hundred parts is, to say the least, rational, whereas in our

F. scale this same interval is divided into 180 parts and the zero is 32° below freezing. This point was originally founded on a scientific hypothesis which has, however, since been proved incorrect. When all has been said in the favour of the Fahrenheit scale, however, it is not comparable for simplicity with the Centigrade.

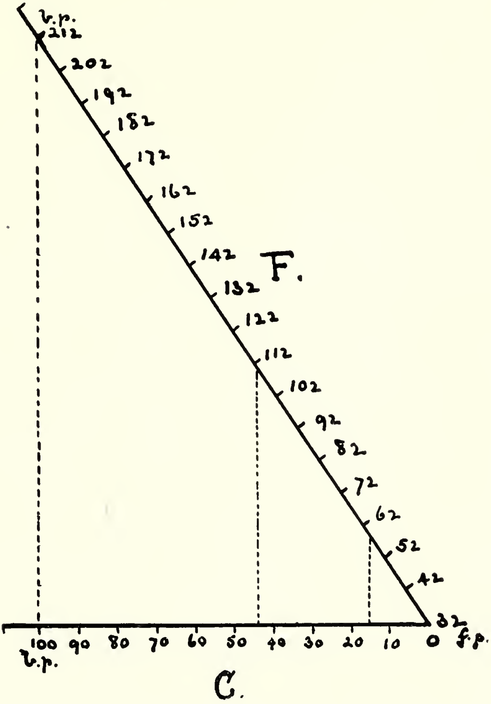


FIG. 4.

Fig. 4 shows a mechanical method of determining what a temperature in one scale would be in the other, by simply drawing a perpendicular as shown at 100° (*b.p.*), 112° (F.), and 15° C. (normal temperature). The divisions in the diagram will explain themselves.

I have given this chapter at some considerable length on account of its importance and the confused ideas which most of us have on this subject. I have, however, omitted many interesting points, for enlightenment on which I must refer my readers to some good text-book on Arithmetic.

CHAPTER IV.

MANIPULATIONS.

I SHOULD recommend every photographer to obtain at least a few feet of small soft glass tubing, and the same of solid glass rodding ; a dozen test tubes (tubes of very thin glass closed at one end) ; two or three beakers, which are glasses made of very thin material, that can be placed over a flame and the contents boiled ; three glass funnels, small, medium, and large size ; and a small spirit lamp. The whole of the preceding should not cost more than about two shillings or half a crown. It will be surprising how useful these things will be to a photographer ; especially one who has to work under difficulties in a scullery, or suchlike place. Moreover, their cost will be saved over and over again by making up one's own solutions, instead of buying them ready for use.

Stirring rods.—Take the solid glass mentioned above and scratch with a file into lengths of about six inches ; a sharp bend with the two hands, one on each side of the scratch, will cause it to break quite evenly. The ends of these rods should be rounded off by holding one end at a time in a gas or spirit lamp flame until of a nice round shape, then allowed to cool slowly. These things will be found very useful to assist solution, especially of such substances as amidol in sodium sulphite solution, etc.

Dropping tubes can be very easily made. Heat a piece of glass tubing of small bore in a flame until soft, then remove from the source of heat and gently pull out until the constriction is of the size required, allow to cool and cut off with a file as explained for rodding. The pieces are finished by affixing a baby's teat to the larger end.

Bending glass tubes.—Cut off the required length of tubing and hold across the widest part of an ordinary fishtail burner just above the non-luminous portion. Keep rotating the tube until it softens and bends by its own weight; then bend into required shape, and allow to cool with the black on it; when cold wipe, and the tube will be found to be bent in a graceful form.

Filtration.—Most soluble chemicals contain insoluble impurities, small particles of dirt, dust, and other foreign matter. When a solution is made of such a substance these impurities remain suspended in the liquid, and must be removed by filtering. The best way is to get a glass funnel and support it in some way over the bottle in which the solution is to be stored; in the funnel is placed a piece of blotting paper folded as described below. Into this pour a portion of the liquid, and allow to percolate through, pouring more into the funnel from time to time till finished.

Filter papers.—Circles varying in size from two to six inches in diameter, according to the size of the funnel, and the amount to be filtered, can be cut out of ordinary blotting paper or bought ready cut in packets for a few pence. One of these circles is taken and folded in two across the middle, again across the middle, opened as shown in fig. 5 and put in the funnel.

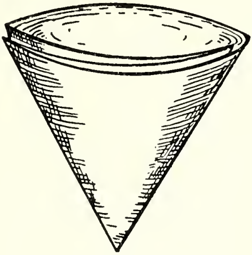


Fig. 5.

Spatula.—A very handy form of spatula can be made from an old thick film and a penholder. Cut the film into an oblong, one and a half inch wide and about two inches long, insert one of the narrow ends into a slit in the top of the penholder, bind with a piece of cotton, and the thing is finished.

CHAPTER V.

SOLVENTS AND SOLUTION.

The greatest solvent known to the chemist is water. It will dissolve to a greater or less extent almost every known substance, and this simple fact is the cause of much worry to the photographer. It is not what the water dissolves after manipulation is commenced, but what it has come in contact with previous to being drawn from the water tap. Rain water is the original source of all our supplies, and in this form, if collected from clean surfaces, it is an admirable substitute for distilled water, as it contains very little, if any, dissolved matter. Sir W. Abney, in his "Text-book of Photography," puts rain water last, on account of the organic matter it contains; but I cannot agree with him, as I have always found that filtered rain water is much the best to use. If our supply is from a well, the rain water gets there by percolating through the various soils, rocks, etc. According to the character of the medium through which it passes, so the water is unsuitable for this or that process. I shall show how to detect these impurities, and explain how they act on various photographic chemicals ; and it comes to this, that the chapter will deal with our greatest of solvents—Water. I must impress on my readers the importance which they should place on its purity. As water occurs everywhere, and often where it is not wanted, all waters are looked upon as much the same. Most books on photography pass this liquid over in a much too superficial manner, and I am convinced that a large proportion of the apparently inexplicable vagaries met with in the course of photographic work is due solely to the water used in making up the solutions, or even in washing.

Rain water when collected in large towns is found to be more or less slightly contaminated with ammoniacal salts, sulphuric acid, hydrochloric acid, nitrates, sulphates, etc., due to the dissolving by the rain-drops of the dust particles in the atmosphere. It will thus be obvious that for photographic purposes the first portions of a shower should be rejected, and only the latter portions collected, which will be found much purer, and in fact suitable after filtration for use in making stock solutions, etc. The average amount of dissolved matter found in the rain water of towns is about 3 parts in 100,000, and in the country much less than this.

Spring and well water is simply rain water after it has sunk into the crust of the earth and collected in some natural or artificial depression. The nature of the contamination which a rain water will suffer depends to a great extent on the nature of the geological strata through which it passes, and also on the rate at which percolation takes place. The hardness of a water is due to the amount of calcium and magnesium salts in solution. When these consist of the carbonates chiefly of the former, they can be softened by boiling, the carbonates being precipitated.

$$\underset{\substack{\text{Soluble}\\ \text{calcium carbonate}}}{CaH_2(CO_3)_2} = \underset{\substack{\text{insoluble}\\ \text{calcium carbonate}}}{CaCO_3} + \underset{\text{water}}{H_2O} + \underset{\substack{\text{carbonic}\\ \text{acid gas}}}{CO_2.}$$

From the above equation it will be seen that the $CaCO_3$ is kept in solution by the carbonic acid gas forming a calcium bicarbonate salt, which is decomposed on heating. This is known as temporary hardness. If, however, the salts consist of the sulphates or chlorides of these elements, boiling will not precipitate them, and hence these waters are known as permanently hard.

The water in my neighbourhood is exceptionally hard, caused by passing through layers of chalk, which is chemically the same as limestone or calcium carbonate. Suppose I were to make up my platinotype developing solution with this water I would get a very dense white precipitate of calcium oxalate as follows :—

$$\underset{\substack{\text{Calcium}\\ \text{bicarbonate}}}{CaH_2(CO_3)_2} + \underset{\substack{\text{potassium}\\ \text{oxalate}}}{K_2C_2O_4} = \underset{\substack{\text{calcium}\\ \text{oxalate}}}{CaC_2O_4} + \underset{\substack{\text{potassium}\\ \text{carbonate}}}{K_2CO_3} + \underset{\substack{\text{carbonic}\\ \text{acid gas}}}{CO_2} + \underset{\text{water.}}{H_2O.}$$

Now, this would in more ways than one seriously affect the developing of platinotype prints. It can, however, be overcome by thoroughly boiling the water and filtering, or instead of filtering allowing it to stand, and when all the precipitated chalk has settled, decanting off the clear liquid.

Chlorides are always found, in smaller or larger quantities, in all natural waters. This is an impurity which precipitates silver salts from their solutions, and in any quantities more than the merest trace is particularly obnoxious when dealing with sensitising solutions. Traces of organic matter in waters are for most purposes not of much importance. When making gold chloride solution, however, distilled water should always be used, otherwise a good deal of the gold will be precipitated, and be lost for toning.

To test the suitability of a water for photographic purposes, take four test tubes, each about one-third full, and add to—

1. A few drops of silver nitrate ($AgNO_3$) solution. Not more than a slight opalescence should be visible, otherwise there is too much chloride for our purpose.
2. A few drops of barium nitrate ($Ba2NO_3$) solution. Only a very slight precipitate should be visible, otherwise the sulphates are excessive.
3. A few drops of a weak soap solution will give a lather after being vigorously shaken, unless the water is excessively hard.

4. After boiling with a drop of pure, concentrated nitric acid (HNO_3) and cooling, no red coloration should be produced on the addition of a solution of potassium sulphocyanide, showing the absence of iron in solution.

Washing waters, I am afraid, must be taken as found, as it would be beyond the ordinary mortal to chemically treat such large quantities. If there is any suspended matter, which the great majority of waters have, the best thing to do is to tie a piece of flannel or swansdown calico round the tap, and one will be surprised at the amount of dirt thus arrested.

Solubility.—Many people confuse solubility with rate of solution. The solubility of a body at any temperature is the amount which will be dissolved by 100 grammes of the liquid at that temperature. The rate of solution depends, not on its chemical properties, but on its physical condition. For example, sodium sulphite will take some considerable time to dissolve when in the form of large crystals, but the same amount will dissolve very much quicker if it is first ground to a powder; the amount finally dissolved being identical in the two instances. A good method for showing the solubility of various bodies is by means of curves. Draw a line AB (fig. 6), mark off into, say, ten equal parts, and let each division equal ten degrees Centigrade, then draw AC at right angles to AB, and divide off into, say, twelve equal parts, and let each division equal ten parts of a substance, number as shown in the

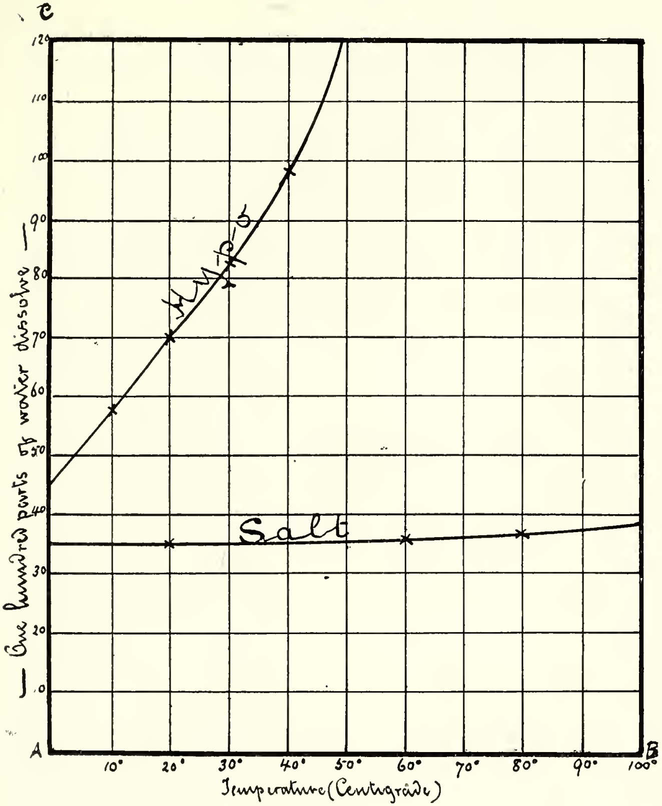


FIG. 6.

diagram. We get the curve of solubility for common salt (NaCl) from the following data, which gives the amount dissolved by one hundred parts of water.

100 parts of water at 0° dissolve 35·6 parts of NaCl.
” ” ” 20° ” 35·9 ” ”
” ” ” 60° ” 37·1 ” ”
” ” ” 80° ” 38·0 ” ”

We go along AB till we come to 20°, then follow the upward line till opposite 35·9 on AC, shown by a cross. The same thing is done at 60° and 80°. The little crosses are then joined together by a curve starting from 35·6 on AC, which in this case is almost a horizontal straight line, showing that the solubility is only very slightly increased by heat. Hypo increases very rapidly in solubility when heated, as will be seen by the shape of the other curve in fig. 6. The data from which the curve is drawn being 100 parts of water, dissolve at

0°, 47·6 parts of sodium thio-sulphate.
10°, 58·0 ” ” ”
20°, 69·0 ” ” ”
30°, 82·0 ” ” ”
40°, 98·0 ” ” ”
47°, 114·0 ” ” ”

In fig. 7 the curves of some common chemicals which the photographer uses are given. By means of these curves the solubility of the substance can be obtained for any temperature by simply drawing lines parallel to AB and AC respectively. Most substances in the process of dissolving absorb heat, and hence lower the temperature of the whole ; thus, by their own action, making solution more difficult and slow. Hypo, if put into a beaker of warm water

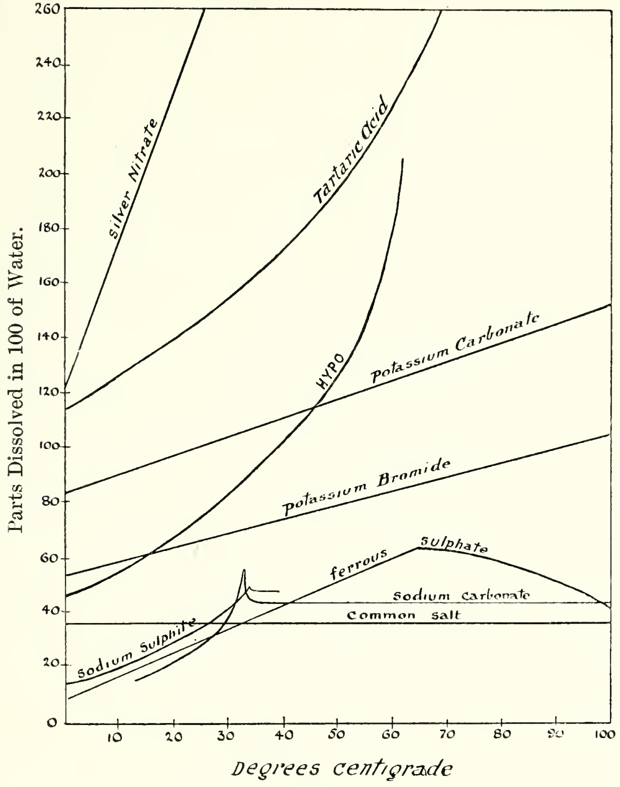


FIG. 7.

and stirred, will be found to get cold almost immediately. Hence the object of warming a liquid to aid solution. An exception to this rule of absorbing heat is caustic soda and potash, which give out much heat in the process of dissolving.

True solution takes place when a body undergoes no chemical change in the process. Silver does not dissolve in nitric acid, but decomposes the acid, forming silver nitrate, which is dissolved in the remaining acid and water.

Percentage Solution.—What is understood by a 10 per cent. solution? Accurately this means a solution, 100 grammes of which contain 10 grammes of the solid. This would necessitate weighing liquids, which is very inconvenient, and to simplify matters we use a combination of weighing and measuring. Take 10 grammes of the solute and make up to 100 c.c. with the solvent (this is very different to adding 100 c.c.). The result will be a solution containing what is known as 10 per cent. of the solute whatever it is.

If there is water of crystallisation with the solid, as, for example, $Na_2SO_3-7H_2O$, a 10 per cent. solution means 10 grms. of crystallised sulphite, including the seven molecules of water, made up to 100 c.c. with water.

CHAPTER VI.

SENSITISERS.

In this chapter I shall deal with a few chemicals of very different natures, which are in some way connected with sensitising emulsions on papers and plates.

Silver is a soft white metal, obtained largely from galena, the chief ore of lead; it is obtained as a bye product. Pure silver can be best obtained from its waste solutions, or old silver dissolved in nitric acid, then precipitating with hydrochloric acid or common salt. The precipitate is washed thoroughly by decantation. The silver chloride thus obtained is boiled gently with caustic soda solution for an hour, adding every few minutes small quantities of glucose. The liquid will become a dirty brown, and the reduced silver chloride will settle to the bottom, and is washed with water first by decantation, and finally on a filter paper. The appearance of the metal in this state will differ very little from the original chloride. After drying, this " molecular " silver, as it is called, should be fused until all the metal runs into a button on a little cupel made of bone ash, which absorbs any lead which might be present. This is a good method for recovering silver from photographic waste, and one will be surprised at the amount that can be thus recovered (see Appendix VI.).

Silver nitrate ($AgNO_3$) can be obtained by dissolving the silver bead obtained above, in nitric acid,

$$Ag_2 + 2HNO_3 = 2AgNO_3 + H_2,$$

and evaporating down to a very concentrated solution, and allowing the salt to crystallise out, but better to evaporate to dryness, and fuse in a porcelain dish over a flame. A crystal is shown in fig. 8. Silver nitrate is very soluble in water, as will be seen by referring to its curve in fig. 7. 100 parts of water at 100° C. dissolve over 900 parts of this salt. It should be perfectly neutral to litmus test papers. It is not likely to be alkaline, but might possibly be acid, in which case it would turn blue litmus red.

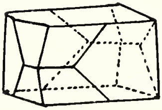


FIG. 8.—CRYSTAL OF SILVER NITRATE.

Litmus papers are small strips of blotting paper soaked in a vegetable extract called litmus, either slightly acidified or made alkaline, and then allowed to dry.

An acid turns blue litmus red.

An alkali turns red litmus blue.

Silver haloids (chloride, bromide, and iodide, AgCl, AgBr, AgI) are very similar in their actions and preparations, and will be treated here together. They are prepared by the action of the respective soluble haloid salts or acids on a solution of silver nitrate, which would be in the case of the chloride with common salt :—

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

and bromide with hydrobromic acid :—

$$AgNo_3 + HBr = AgBr + HNO_3.$$

The chloride is thrown down as a white curdy precipitate, soluble in aqueous ammonia, whereas the bromide is very pale yellow and only slightly soluble, and the iodide is yellow and insoluble. All three are insoluble in water, and, of course, soluble in sodium thiosulphate (hypo), but this will be dealt with in a later chapter.

When silver chloride in water is exposed to light, it very soon darkens, and after a time free hydrochloric acid (HCl) will be found in the liquid, and metallic silver along with the chloride. Carey Lea put this darkening down to various subhaloids or oxyhaloids, which he called "Photo-salts." Space, however, prevents me discussing this here. The following table will be found of use, and gives the equivalent of the various silver salts; 1 gramme or grain of silver gives 1·57 grammes or grains of the nitrate, and 1 part of nitrate contains ·635 part of silver, and so on.

Table of Equivalents of Silver Salts.

Silver.	Nitrate.	Chloride.	Bromide.	Iodide.
1	1·574	1·328	1·741	2·176
·635	1	·844	1·106	1·382
·752	1·184	1	1·310	1·638
·574	·904	·763	1	1·250
·460	·723	·610	·800	1

Bichromate of potash ($K_2Cr_2O_7$) is used for sensitising carbon tissue and gum. It is manufactured from chrome iron ore by roasting, and after passing through a variety of processes, which my readers could not repeat on a small scale, potassium chromate is obtained. This is then treated with the requisite amount of sulphuric acid (98 parts of acid to 388 of chromate), which can be calculated from the equation by the process shown in Chapter II.

$$\underset{\text{Potassium chromate}}{2K_2CrO_4} + \underset{\text{sulphuric acid}}{H_2SO_4} = \underset{\text{potassium bichromate}}{K_2Cr_2O_7} + \underset{\text{potassium sulphate}}{K_2SO_4} + \underset{\text{water.}}{H_2O,}$$

The bichromate, or, to be strictly accurate in nomenclature, di-chromate, is much less soluble in water than the chromate, consequently most of it is precipitated, and if well stirred during the process the crystals are very small indeed, and would thus contain little, if any, impurity in the interior of the crystals. These should be placed in a filter and washed several times with small quantities of pure water ; some will of course be dissolved, but all the free acid will be removed, which is a very objectionable impurity; it can be further purified by recrystallising from a fresh solution.

In the carbon process the gelatine and pigment, after being spread on paper, is soaked in a solution of bichromate, and dried in the dark. When exposed to light the CrO_3 of the bichromate is reduced to the basic oxide (Cr_2O_3), and simultaneously the gelatine is made insoluble, possibly by the formation of formaline, which in its turn acts on the gelatine.

Ferric oxalate is prepared by dissolving 30 grammes of iron piano wire in nitric acid by gentle heat, then adding an equal quantity of strong ammonium hydrate until it smells strongly of the gas. The brown precipitate of ferric hydrate is washed by decantation, and 100 grammes of crystallised oxalic acid is added, and thoroughly shaken till dissolved.

$$\underset{\text{Ferric hydrate}}{Fe_2(OH)_6} + \underset{\text{oxalic acid}}{3H_2C_2O_4} = \underset{\text{ferric oxalate}}{Fe_2(C_2O_4)_3} + \underset{\text{water.}}{6H_2O.}$$

This last operation should be performed in artificial light; filter, and make up to 600 c.c. This gives a solution containing, approximately, 20 per cent. of ferric oxalate; and is the strength generally used in making platinotype paper.

Ferric oxalate when in very thin layers is acted on by light, being reduced to ferrous oxalate thus:—

$$Fe_2(C_2O_4)_3 = 2FeC_2O_4 + 2CO_2.$$

Potassium chloro-platinite (K_2PtCl_4) is a salt used in sensitising platinotype paper along with the compound previously described. It can be prepared by heating platinic chloride ($PtCl_4$) to about 300°, C. $PtCl_4 = PtCl_2 + Cl_2$, when platinous chloride is the result. By the action of hydrochloric acid on this latter substance, chloro-platinous acid (H_2PtCl_4) is formed. If a solution of potassium chloride (KCl) is now added, K_2PtCl_4 crystallises out.

When light acts on the platinotype paper reduction of the ferric oxalate takes place, as shown above; this latter is soluble in a solution of potassium oxalate. While going into solution, however, to reform ferric, the ferrous oxalate reduces the potassium chloro-platinite, precipitating the platinum which gives the image.

$$3K_2PtCl_4 + 6Fe(C_2O_4) = 3Pt + 2Fe_2(C_2O_4)_3 + Fe_2Cl_6 + 6KCl.$$

Ferric ammonium citrate is obtained in the form of scales. It is prepared in the following manner:—

Take a known quantity of ferrous sulphate ($FeSO_4$), and place in a beaker of water; add a few drops of strong nitric acid, and boil for some time, then add ammonia till smelling strongly of it, wash the precipitated ferric hydrate ($Fe_2(OH)_6$) thoroughly, place in a beaker, and add a solution of citric acid until just dissolved, and mix with this the same amount of citric acid as already used, previously neutralised with ammonia; evaporate to dryness, and then spread on sheets of glass to dry.

This forms the brown salt used in medicine, but there is a green modification which is much more sensitive to light.

Silver gallo-nitrate is a sensitiser for colotype paper. It is not a true chemical compound, but a mixture made up as follows:—7 grammes of silver nitrate ($AgNO_3$) dissolved in 60 c.c. of water, and 10 c.c. of glacial acetic acid added; just before use mix with 70 c.c. of a saturated solution of gallic acid.

Ferric chloride (Fe_2Cl_6) can be prepared by dissolving ferric oxide in hydrochloric acid. The anhydrous salt is of a very dark colour, but when allowed to crystallise from an aqueous solution yellow crystals are formed having the formula (Fe_2Cl_6—$12H_2O$).

Cuprous chloride (Cu_2Cl^2) can be precipitated as a white powder by passing sulphur dioxide gas slowly through a solution of cupric chloride thus:—

$$2CuCl_2 + SO_2 + 2H_2O = Cu_2Cl_2 + 2HCl + H_2SO_4.$$

It is very easily soluble in ammonia, giving a colourless solution, turning blue in contact with the air, owing to the re-formation of cupric chloride.

CHAPTER VII.

DEVELOPERS.

The nature of the latent photographic image is still problematical. Within the last few years many new theories have been evolved, and old ones rejuvenated.

A Physical Change theory has been brought forward, but I am afraid that the definitions on which this theory is elaborated are not perfectly sound. Perhaps these definitions are passable from a popular point of view; but to build highly scientific theories on a popular non-exact scientific definition is, to say the least, building a house on a foundation of sand.

A Chemical Change theory is the one generally accepted at the present day. Of the chemical theories, the sub-bromide one is the oldest and most widely accepted.

When a photographic dry plate is exposed to the action of light, the silver bromide (argentic bromide) is split up on the surface, in *very* minute quantities, into bromine and silver sub-bromide (argentous bromide) thus:—

$$\underset{\text{Argentic bromide}}{2AgBr} = \underset{\text{argentous bromide}}{Ag_2Br} + \underset{\text{bromine.}}{Br.}$$

The action of the developer is, then, simply to further reduce the silver sub-bromide to metallic silver. This is, of course, the old theory of many years ago. The newer part is the way in which the *immensely* large proportion of silver in the developed image is accounted for, as compared with the minute quantity of partially reduced silver bromide (*i.e.*, sub-bromide) in the plate as originally exposed. The supposition is that the silver sub-bromide gives, on development, the silver in a nascent or atomic state. This silver being in contact with further portions of silver bromide immediately combines with these, reducing them to the sub-bromide. The two steps may be shown by equations, thus :

I. $Ag_2Br + \text{Devel.} = 2Ag + Br + \text{Devel.}$

II. $2Ag + 2AgBr = 2Ag_2Br.$

We thus get a continuous cyclical action during development. Whether the bromine is absorbed by the developer or by the gelatine is quite immaterial to the above.

With the proviso that only a portion, say half, of the reduced silver is used in reducing further quantities of the silver bromide, this theory would explain the formation of a large quantity of metallic silver from an infinitely small amount of silver sub-bromide. Further, this theory would explain why an image "comes up" faster after the first portions have shown themselves. The fact that an image begins to show itself only some time after the developer has been poured on would be explained by the original amount of the sub-bromide being so very minute that all the silver first reduced would be used up in reducing silver bromide according to equation II., and not being deposited in the film. Over-exposed plates would, for the same reason, come up quickly, and under-exposed slowly. On the other hand, how would reversal be explained? Again, argentous bromide has never been formed in any other way, and its presence in an exposed photographic plate has never been experimentally shown.

I see no scientific reason why the silver bromide and gelatine should not, under the action of light, unite to form a new compound. It is a well-known fact in chemistry that by adding to certain parts of an organic radicle, by the process, as it were, of altering the equilibrium of the molecule, the original part can in many cases be split up more easily than without the addition. Light impinging on the film supplies enough energy to form this complex compound more or less throughout the thickness of the film. It is then found that the developer has the power of splitting up this new substance and depositing metallic silver, but it had not the power of decomposing the original silver bromide, except very slowly.

I anticipate the objection that the gelatine film has been analysed, and no such compound has ever been found. It must, however, be remembered that, according to this theory, we have a molecule so elaborately and yet so delicately constructed, that even the slightest alteration in its environments may break up the whole combination. Its contact with most substances would have a similar effect, that of rendering the complex molecule into its *original* constituents. Developers, however, are characterised by their power of splitting it up into *different* constituents—*i.e.*, depositing the silver. Too much energy, in the form of light, could, I think, be easily imagined to produce a like result. Hence, on this hypothesis, the phenomena of reversal might be easily explained.

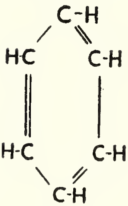
Considering the little, or, I may even say, the next to nothing, we know about the chemistry of gelatine and other complex natural organic bodies, it is no wonder that there has not yet been evolved a satisfactory chemical theory of the developable image. I don't wish to suggest that a physical theory is absolutely untenable, but I certainly think that a chemical one is much more probable, or even, as has been suggested, a physico-chemical change. To properly appreciate these abstruse theories, one must have a rather profound knowledge of physics and chemistry, and it is the author's hope that this book may be the means of some taking up the study of chemistry, who would not otherwise have done so.

The following portion of the chapter I propose dividing into three parts.

A. Developers Proper are bodies which are easily oxidised, and which have a preferential action on silver haloids, reducing those parts on which light has acted, and having very little effect on the parts not thus acted on. During this process the developer reduces the silver salts and deposits the metallic silver in the medium in which it was held, and at the same time being itself oxidised.

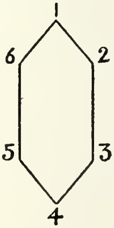
From the above definition of a developer it is obvious that every compound to be thus classed must have some particular grouping of the various atoms in the complicated molecules of which they are made up. As an introduction to the developers, I will give some details concerning the parent of nearly all developers—Benzene.

Benzene is obtained by the distillation of coal tar, etc. Its formula is C_6H_6, but to distinguish this substance we must show graphically how the six



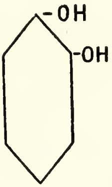
(1)

(2)

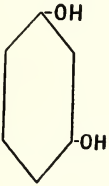


(3)

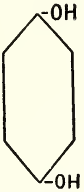
carbon atoms are joined in a ring. (1) shows this in full, but for simplicity it is represented as (2), the C and H atoms being supposed to be at each corner; its simplicity will be apparent when we come to discuss the derivatives. In order to show in which position any addition is made to a benzene ring, we number each carbon atom as shown in (3). An example will make this plain. If one H were replaced by hydroxyl group (OH), we should have phenol, or carbolic acid, and as only one would be replaced, it would be immaterial which. When, however, two hydrogen atoms are replaced by (OH) groups, then it is essential to know which position they occupy.



Catechol



Resorcinol



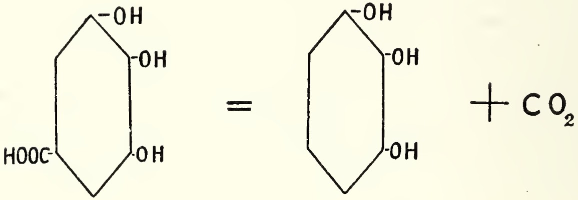
Hydroquinone

1 : 2 would be the same as 1 : 6, and is known as the ortho-position. 1 : 3, same as 1 : 5, or meta-; 1 : 4 being the para-. Hydroquinone may thus be written as para-dihydroxy-benzene, or para-hydroxy-phenol; resorcinol or resorcin as meta-dihydroxy-benzene or meta-hydroxy-phenol; catechol or pyro-

catechin as ortho-dihydroxy-benzene or ortho-hydroxy-phenol.

When three hydrogens are replaced, these equalities do not hold good.

Pyro is the short for pyrogallol, or pyrogallic acid, and is a 1 : 2 : 3 trihydroxybenzene, and would be represented graphically as shown in the equation below. It can, as its last name implies, be obtained by heating gallic acid either alone or along with glycerine, to between 200° and 215° C., until no more carbonic acid gas is given off:—



Gallic Acid *Pyro* *Carbonic acid gas*

It is a white crystalline body, which melts at 115°, and is very soluble in water, and is most easily purified by sublimation. When oxidised it forms acetic and oxalic acids; these are not formed in development. As we have excess of sodium carbonate, we get sodium acetate and oxalate formed, besides other compounds of a dark colour, such as meta-gallic acid, which is insoluble in water.

Hydroquinone, or quinol ($C_6H_4(OH)_2$), and has the graphic formula shown above. It is prepared from aniline ($C_6H_5NH_2$), which is an amido compound derived from benzene, by oxidising with potassium bichromate and sulphuric acid. A yellow crystalline substance crystallises out, known as quinone ($C_6H_4O_2$). If this substance be now dissolved in water and sulphurous acid added, or sulphur dioxide gas passed through, hydroquinone is formed :—

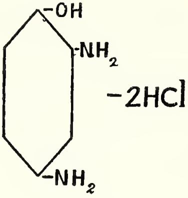
$$C_6H_4O_2 + H_2SO_3 + H_2O = C_6H_4(OH)_2 + H_2SO_4.$$

The solution is then shaken up with ether, allowed to settle, and the water run off. The ether extracts all the products of reduction, which on evaporation leaves the hydroquinone as a white solid, melting at just under 170°.

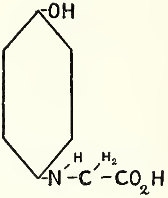
Amidol—2 : 4 diamido-phenol hydrochlorate ($C_6H_3OH(NH_2)_2$—$2HCl$)—is prepared by reducing a body very nearly related to picric acid, namely, dinitro-phenol by means of hydrochloric acid and tin. It is a white crystalline body, very soon darkening when exposed to light and very soluble in water. On the application of heat it decomposes before melting.

Glycin—para-oxyphenyl glycin, or para oxyphenyl amido acetic acid, consists of white crystals of a plate or scale form. It is prepared by the action of chloro-acetic acid on para-amido phenol.

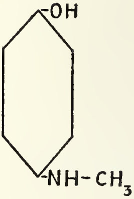
Metol is sulphate of methyl para-amido phenol, it crystallises in white prisms or needles. Metol is very closely related to glycin, as will be seen from the following graphic formulæ :—



Amidol



Glycin



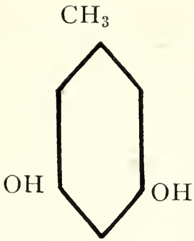
Metol (base)

Ortol is a compound developer, being a mixture of methyl-ortho-amido-phenol sulphate with hydroquinone.

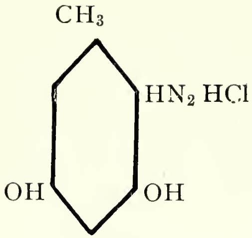
Para-amido-phenol is the hydrochlorate of 1 : 4 amido-phenol, and is prepared by reducing para-nitrophenol with tin and hydrochloric acid. It crystallises in white prismatic crystals. The free base, however, forms crystalline plates.

Rodinal is a highly concentrated solution of the previous developer, to which an alkali and neutral sulphite has been added, the alkali being only sufficient to form a salt with the developer proper.

Synthol is a new developer, and is the hydrochloride of diamido-orcinol. The parent substance orcinol or orcin is obtained from many kinds of lichens. Synthol is very soluble in water, slightly so in alcohol, and insoluble in ether and benzene, and



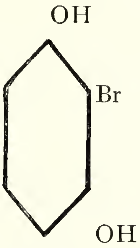
Orcinol



Synthol

according to W. Thomas, F.R.P.S., is an English made developer.

Adurol is a mono-bromo-substituted product of hydroquinone. It occurs as a white crystalline powder, soluble in water, and very soluble in alcohol and ether.

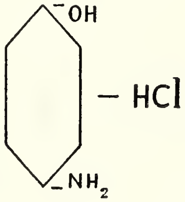


Adurol

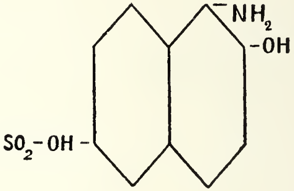
Pyrocatechin, or catechol ($C_6H_4(OH)_2$), is isomeric with hydroquinone and shown above. It can be prepared by heating guaiacol with hydriodic acid, or by the dry distillation of catechu itself obtained from various Indian trees. It is a colourless crystalline body, melting at 104°, very soluble in water.

Diogen—a developer similar in composition to eikonogen.

Eikonogen does not belong to the same family as the above developers. It has a double ring, as shown below, and is a sodium salt of *α* amidol- *β* naphthol sulphonic acid.



Para-amido-phenol



Eikonogen

Edinol is one of the new developers quite recently brought out. It is generally supposed to be ortho-amido-meta-oxy-benzyl alcohol, and would consequently differ considerably from the other developers considered above. Edinol is a light brown powder very soluble in water.

Carbamide or urea (CH_4N_2O) is a substance which is said to have developing powers ; not strong ones but nevertheless capable of developing a photographic image. It can be formed by heating ammonium cyanate, a body having the same per centage composition, but with a different molecular arrangement.

$$\underset{\substack{\text{Ammonium}\\ \text{cyanate}}}{NH_4CNO} \quad = \quad \underset{\text{carbamide.}}{\begin{matrix}NH_2\\ NH_2\end{matrix} > CO.}$$

Hydroxylamine (NH_2-OH) is known as an odourless solution which gives an alkaline reaction. It can be prepared by reducing nitric oxide with nascent hydrogen made by the action of an acid on zinc thus :—

$$Zn + 2HCl = ZnCl_2 + 2H.$$
$$NO + 3H = NH_2-OH.$$

It can also be prepared by reducing ethyl nitrate ($C_2H_5NO_3$).

Hydroxylamine hydrochlorate ($NH_2OH-HCl$) is obtained in the solid form by neutralising the solution obtained in the previous reaction with HCl and allowing to crystallise.

Hydrazine (N_2H_4) is a compound which can only be prepared by very complex reactions. It is very similar to ammonia in its properties.

Potassium oxalate ($K_2C_2O_4-H_2O$) is a poisonous white crystalline substance obtained on concentrating a solution of oxalic acid neutralized with caustic potash (KOH).

Ferrous oxalate (FeC_2O_4) is generally prepared as wanted by adding ferrous sulphate solution to a solution of potassium oxalate. It is insoluble in water, but dissolves in potassium oxalate, hence double the amount of this salt must be added in order to keep the ferrous oxalate formed in solution thus :—

$$FeSO_4 + 2K_2C_2O_4 = FeC_2O_4 + K_2C_2O_4 + K_2SO_4.$$

When in a dry state ferrous oxalate consists of a light yellow powder.

Ferrous sulphate is obtained by dissolving iron in sulphuric acid, the solution evaporated down, when this substance crystallises out in pale green monosymmetric crystals having the formula $FeSO_4—7H_2O$, which effloresce when exposed to the air.

B. ACCELERATORS and various adjuncts to the developer proper will be treated in this part of the chapter.

Carbonate of soda is manufactured from common salt by one of two methods. 1. *The Leblanc process.* Salt is treated with sulphuric acid, forming sodium sulphate, or "salt cake." The resulting mass is mixed with coal (for its carbon) and limestone ($CaCO_3$), and strongly heated in a revolving furnace when the following change takes place :—

$$Na_2SO_4 + 2C + CaCO_3 = Na_2CO_3 + CaS + 2CO_2.$$

This mass, known from its colour as "black ash," is lixiviated with water, which dissolves the carbonate and leaves the calcium sulphide as an insoluble residue. The liquor is allowed to settle, then drawn off and evaporated down, when "soda crystals"

($Na_2CO_3—10H_2O$) separate out. The crystals are sometimes calcined, which leaves "soda ash," or anhydrous sodium carbonate. This process is much more expensive than the next one to be described, and would not be used now but for the valuable bye-product which is obtained, namely hydrochloric acid, as explained in the next chapter. 2. *The ammonia soda process* consists of forcing carbon dioxide gas under pressure through a solution of salt saturated with ammonia gas, first forming ammonium carbonate, and then reacting on the salt according to the two following equations :

$$2NH_3 + CO_2 + H_2O = (NH_4)_2CO_3$$
$$(NH_4)_2CO_3 + NaCl = NaHCO_3 + NH_4Cl + NH_3.$$

The bicarbonate of soda thus formed being only sparingly soluble in water separates out. If the carbonate is required this is heated and "soda ash" is the result. The solubility of sodium carbonate reaches a maximum at 32·5°, when on further heating the solubility rapidly falls away ; *vide* fig. 7. A crystal of washing soda is shown in fig. 9 ; it belongs to the monoclinic system.

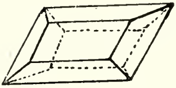


Fig. 9.—Crystal of Sodium Carbonate.

When a solution of a certain percentage strength is required in photography the percentage of crystals is meant, not of the anhydrous sodium carbonate. It will be seen, on referring back to the end of Chapter II., that 286 parts of soda crystals contain 180 parts of water and 106 of anhydrous carbonate; hence a 10 per cent. solution, as we understand it, contains only 3·7 per cent. of Na_2CO_3.

There are several forms of sodium carbonate. There is the anhydrous carbonate mentioned above (Na_2CO_3), with no water of crystallisation, which is very similar in appearance to the bicarbonate; they can, however, be easily distinguished by the second test given below. When soda crystals ($Na_2CO_3—10H_2O$) are exposed to the air they effloresce; that is, some of the water of crystallisation is given off and a new substance ($Na_2CO_3—H_2O$) is formed and appears as a white powder on the crystals. This body it will be noticed from the formula contains a larger per centage of anhydrous carbonate than the crystals do. Hence in weighing, care should be taken that as little as possible of this substance is weighed, otherwise your solution will be stronger than you intended it to be.

Sodium bicarbonate ($NaHCO_3$) is a substance sold by chemists and grocers as "carbonate of soda" for culinary purposes. This stuff is, however, absolutely useless for developing. Always go to a photographic chemist for carbonate of soda crystals, or to the grocer for ordinary washing soda, and pick out the bright and clear crystals, and make up your solution in the ordinary way and filter. This will be found quite good enough for ordinary work.

Suppose that by some mischance one finds himself with only bicarbonate of soda, the omission can soon be remedied. If a solution of bicarbonate of soda be boiled, we get the carbonate formed as follows :—

$$\underset{168}{2NaHCO_3} = \underset{106}{Na_2CO_3} + \underset{18}{H_2O} + \underset{44}{CO_2}$$

If these amounts be calculated out as shown in a previous chapter it will be found that 168 parts of sodium bicarbonate yield 106 parts of the anhydrous carbonate. Suppose a 10 per cent. solution of the crystals is required—I have shown above that it is equal to nearly 3·7 per cent. of Na_2CO_3, or 3·7 parts in 100—now by simple proportion the amount of bicarbonate equivalent to 3·7 parts of carbonate can be calculated :—

$$106 : 3{\cdot}7 = 168 : x$$
$$x = \frac{168 \times 3{\cdot}7}{106} = 5{\cdot}86.$$

So if we take 5·86 grammes of bicarbonate of soda, place in a vessel with a little water, and boil for a few minutes, then allow to cool and make up to a 100 c.c., we shall get a solution of the same strength as one of 10 per cent. soda crystals, or the hydrated carbonate.

The anhydrous carbonate and the bicarbonate of soda are, as stated above, very similar in appearance. The best and easiest method for distinguishing them is to put a little of the doubtful substance in a test-tube, then pour on from another test-tube, a few c.c. of boiling water. If no effervescence takes place, it is the carbonate ; the bicarbonate would give off many times its own volume of gas (CO_2). The following table will give the various tests to distinguish between these two substances :

TABLE OF DIFFERENCES.

	Sodium carbonate.	Sodium bicarbonate.
1. Proportional solubility in cold water (15°—16°C.)	1 in 2	1 in 11
2. Hot water poured on some of the substance in a glass	No effervescence	Brisk effervescence
3. Solution of Epsom Salts ($MgSO_4$) added to solution of substance ...	White ppt.	No ppt.
4. Solution of mercuric chloride* ($HgCl_2$) added to solution of substance	Reddish-brown ppt.	White † ppt.

Ammonia (NH_3) is a gas which is very soluble in water and is then known as ammonium hydrate (NH_4OH). The strongest solution of ammonia has a specific gravity of ·882, and contains 35 per cent. of NH_3 gas, that is, one litre contains 308 litres of

---

* Mercuric chloride is the same substance as used for mercurial intensification.

† This precipitate is never obtained quite white, and varies in colour within very wide limits, owing to the fact that all samples of commercial bicarbonate of soda always contain more or less of the carbonate.

gas. It is obtained principally from gas tar, or by the destructive distillation of horns and hoofs of animals. It can be very easily prepared by acting on any ammonium salt, such as the chloride known as sal-ammoniac, with lime or caustic soda :—

$$2NH_4Cl+Ca(OH)_2 = CaCl_2+2H_2O+2NH_3.$$

or,

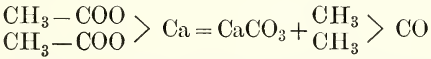
$$NH_4Cl+NaOH=NaCl+H_2O+NH_3$$

ammonia gas being liberated in each case.

Ammonium hydrate should give no precipitate with lime water, showing absence of carbonates, or, with barium nitrate absence of sulphates.

Potassium carbonate (K_2CO_3) was formerly prepared from the ash of plants burnt in pots, hence its name—potash. It is now made almost exclusively from potassium sulphate (K_2SO_4) by a similar process to the Leblanc. Potassium carbonate crystallises with three molecules of water. The anhydrous salt is very deliquescent ; and, as will be seen on referring to fig. 7, very much more soluble in water than the corresponding sodium salt.

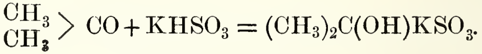
Acetone, or dimethyl ketone $(CH_3)_2CO$, is a liquid, boiling at 56°, miscible with water in all proportions. It is prepared by the dry distillation of crude calcium acetate as follows :—



$$\begin{matrix}CH_3-COO\\CH_3-COO\end{matrix}>Ca=CaCO_3+\begin{matrix}CH_3\\CH_3\end{matrix}>CO$$

Acetone sulphite is a new substitute for alkali and is a compound of acetone and sodium sulphite and bisulphite.

Potassium acetone sulphite is more often known under the name of the previous body. It is supposed to be formed by mixing acetone with a solution of potassium bisulphite, thus :—



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CO + KHSO_3 = (CH_3)_2C(OH)KSO_3.$$

White crystals of this substance separate out.

Sodium sulphite (Na_2SO_3) is prepared by passing sulphur dioxide gas into a solution of sodium carbonate or caustic soda. Take about 100 grammes of sodium hydrate and dissolve in 200 c.c. of water. Divide this solution into two exactly equal parts ; through one of them pass sulphur dioxide until it smells strongly of the gas, then allow to stand for some hours in the warm and most of the odour of burning sulphur has disappeared. The other half of the caustic solution is now added, and the liquid evaporated down to a small bulk and allowed to crystallise. The crystals should be strained and dissolved in a small quantity of warm water and allowed to cool down ; monoclinic crystals separate out, having the formula $Na_2SO_3—7H_2O$. The crystals, if allowed to remain exposed to the air, absorb oxygen,

$$Na_2SO_3 + O = Na_2SO_4,$$

forming sodium sulphate, which is easily detected by the crystals becoming powdery and opaque. A solution of the sulphite becomes oxidised in just the same manner, and takes place the more readily the less there is in the bottle. For further particulars as to its keeping qualities see Appendix VIII.

Nitric acid (HNO_3) is a liquid obtained by distilling nitre with sulphuric acid :—

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

It is a very powerful oxidising agent, and should always be handled with great care.

Sulphurous acid (H_2SO_3) is the solution in water of sulphur dioxide gas, of which it smells strongly. On standing it oxidises, forming sulphuric acid (H_2SO_4) and consequently loosing its odour.

Caustic soda ($NaOH$), or sodium hydrate, is a white deliquescent solid. It can be prepared by boiling a solution of washing soda with excess of slacked lime ; chalk is precipitated, and the caustic obtained on evaporating off the water :—

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3.$$

Potassium meta-bisulphite ($K_2S_2O_5$) is prepared by making a strong solution of potassium carbonate and passing sulphur dioxide gas through until the solution is saturated ; on the addition of absolute alcohol the salt separates out in needle-shaped crystals. These crystals smell strongly of burning sulphur and are thus easily distinguished from the ordinary sulphite.

Tribasic sodium phosphate ($Na_3PO_4—12H_2O$), or normal phosphate, has been suggested by Messrs.

Lumière as a substitute for alkali in developers. It is supposed to give stronger images. The thin six-sided prismatic crystals of this substance give a strongly alkaline solution.

C. RESTRAINERS probably depend for their action on the stability of the compounds they form with the silver haloids.

Potassium bromide (KBr) is formed by adding bromine to a solution of caustic potash :—

$$6KOH + 3Br_2 = KBrO_3 + 5KBr + 3H_2O.$$

The solution now contains potassium bromate as well as bromide. If the solution be evaporated to dryness and then ignited, the bromate is decomposed, the oxygen being given off, and bromide left. The residue should be dissolved in hot water and allowed to cool slowly, when the potassium bromide crystallises out in cubes.

The action of this substance in restraining development is probably due to its forming a more stable salt with silver bromide ; something similar to what takes place when precipitated silver bromide dissolves in excess of potassium bromide.

Ammonium bromide(NH_4Br) is another restrainer prepared in a similar way to the above but using ammonium hydrate instead of caustic potash :—

$$6NH_4OH + 3Br_2 = NH_4BrO_3 + 5NH_4Br + 3H_2O.$$

Its action is similar to the potassium salt.

Sugar is recommended for restraining in the development of one brand of papers. There are many cane sugars chemically known, but take it that ordinary sugar is meant. This has the formula $(C_{12}H_{22}O_{11})_n$ and is obtained mainly from the sugar cane but also from the beetroot.

Citrates. The citrates of the alkalies are used sometimes as restrainers. Any of these can be formed by neutralising a solution of the acid by the respective caustic alkalies. Test with blue and red litmus paper. The solution should then be evaporated down until the salt that is being made crystallises out. Sodium, potassium and ammonium citrate are thus made. The citrates in general use are the three following :—

Ammonium citrate	... ...	$(NH_4)_2HC_6H_5O_7$
Potassium ,,	... ...	$K_3C_6H_5O_7$
Sodium ,,	... ...	$Na_3C_6H_5O_7$

Glycerine will be described in Chapter XIII., as it is not much used as a restrainer except in developing platinotype papers ; in which case its action is more mechanical than chemical.

CHAPTER VIII.

FIXERS.

A FIXING bath is a solution of a substance which will form soluble compounds with the haloid silver salts present in a film, etc., or decomposes them, giving products which are soluble in water. The simplest, cheapest, and most convenient is the well-known "hypo." On account of its importance, and the number of well-known text books in which its action is wrongly described, I think it will be advisable to consider this substance at some considerable length.

"*Hypo.*"—Hyposulphite of soda, or, more correctly, sodium thiosulphate ($Na_2S_2O_3$), was discovered by Chaussier in 1799. It is very soluble in water, from which it crystallises in the monoclinic system (fig. 10) with five molecules of water ($Na_2S_2O_3—5H_2O$). The accompanying diagram was sketched from a crystal formed by allowing an old used plate fixing bath to stand exposed to the air in a porcelain dish. After a week a number of beautiful crystals were formed,

FIG. 10.—CRYSTAL OF HYPO.

which were quite colourless when the dark-coloured mother liquor was poured off.

On a commercial scale sodium thiosulphate is manufactured by boiling sulphur with caustic soda, allowing to settle, and drawing off the solution of sodium sulphide (Na_2S). On passing sulphur dioxide gas through the liquid we get:—

$$Na_2S + SO_2 + H_2O = H_2S + Na_2SO_3.$$

The sulphur dioxide acts further on the sulphuretted hydrogen (H_2S), liberating sulphur, which in its turn acts on the sodium sulphite first formed, thus:—

$$Na_2SO_3 + S = Na_2S_2O_3.$$

From this last equation it will be seen that "hypo" can very easily be made from sodium sulphite by boiling with flowers of sulphur. Should the photographer suddenly find himself without any "hypo," he can soon remedy this if he has any sulphur by him. Make a solution of sodium sulphite, place in a beaker with a little of the powdered sulphur, and boil for a few minutes, filter, cool, and then use for fixing.

Another method of manufacturing "hypo" is by oxidising alkali waste, forming calcium thiosulphate (CaS_2O_3), which is decomposed by a sodium salt, say the sulphate, giving sodium thiosulphate in solution, and precipitating calcium sulphate thus:—

$$CaS_2O_3 + NaSO_4 = CaSO_4 + Na_2S_2O_3.$$

As stated before, sodium thiosulphate crystallises with five molecules of water, and when a certain per cent. solution is mentioned, the crystals are meant. The anhydrous salt can be obtained by heating the crystals to 215° ; at 220°, however, they commence to decompose.

Most of the text books on photography and photographic chemistry have inaccurately given the chemical action of fixing by sodium thiosulphate.

On first putting the plate or print into the fixing solution we get a salt formed consisting of one molecule of silver thiosulphate and one of sodium thiosulphate according to the following equation :—

(I.). $2AgCl + 2Na_2S_2O_3 = 2NaCl + Na_2S_2O_3 — Ag_2S_2O_3$.

This substance is nearly insoluble in water but is soluble in a solution of sodium thiosulphate, forming another double salt with another molecule of the thiosulphate according to equation (II.). This second salt is very soluble, and can therefore be removed by washing the film in water.

(II.). $Ag_2S_2O_3 — Na_2S_2O_3 + Na_2S_2O_3 = Ag_2S_2O_3 — 2Na_2S_2O_3$.

Or to express the whole reaction in one equation :—

(III.). $2AgCl + 3Na_2S_2O_3 = 2NaCl + Ag_2S_2O_3 — 2Na_2S_2O_3$.

Where most of the text books are wrong is in giving the (II) salt as first formed and insoluble and the (I) as soluble. This is obviously wrong if the composition of the two double compounds be carefully examined, remembering the two following well-known axioms for photographers :—

(*a*) *A strong solution of "hypo" fixes quicker and better than a weak one*—because excess of $Na_2S_2O_3$ would tend to more easily form compound (II.).

(*b*) *An old "hypo" solution does not fix as well as a fresh one*—because excess of (II.) salt already in the solution would tend to form with fresh silver haloid the (I.) compound.

To sum up, a weak or a well-used solution of hypo fixes according to equation (I.), whereas a new or strong solution goes like (III.). I have given in these three equations silver chloride, but the iodide and bromide would be dissolved in exactly the same way.

Light always tends to convert the soluble double salt into the insoluble one, hence care should be taken to fix prints and plates in as subdued a light as possible.

Acid fixing bath. This is made by adding to the usual "hypo" bath a small quantity of sodium sulphite solution to which a few drops of strong sulphuric acid have been added, this gives us sulphurous acid, which remains in solution when added to the hypo. This form of bath prevents the staining of prints by the developer. We have all noticed that when an alkali is added to an organic developer the solution soon turns black and stains the fingers or anything put in it. The sulphurous acid neutralises the alkali and in consequence the residual developer in the film remains colourless, and is powerless to stain anything.

Potassium cyanide (KCN) is the potassium salt of prussic acid. It is prepared on a large scale by strongly heating potassium ferro-cyanide :—

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

The carbide of iron (FeC_2) is removed by filtering through heated tiles. The filtrate is run into moulds, and when cold yields a white deliquescent solid, very soluble in water ; it smells of prussic acid, because this acid is so weak that the carbonic acid gas (CO_2) in the air can decompose its salt, liberating the free hydrocyanic acid (HCN). The fixing action of potassium cyanide is as follows :—

$$AgCl + KCN = AgCN + KCl.$$

This gives silver cyanide, which is insoluble in water, but forms with KCN a double cyanide which is soluble :—

$$\underset{\text{Insoluble}}{AgCN} + \underset{\text{soluble}}{KCN} = \underset{\text{soluble.}}{AgCN - KCN.}$$

It is obvious that unless an excess of cyanide is present no fixing takes place. The other silver haloids would give similar reactions.

Note.—This substance must be handled with very great care, as it is exceedingly poisonous. Should any get into an abrasion of the skin rub ferrous sulphate into the affected part.

Ammonia.—An aqueous solution of ammonia gas (NH_4OH) is a solvent for silver chloride ($AgCl$), and hence would fix a film containing that salt. It, however, dissolves the bromide much less, and the iodide only very slightly, and would in consequence be of no use for thoroughly fixing plates.

Sodium sulphite when in strong solutions is also a fixer, but as it is little used for that purpose will not be described here.

Hydrochloric acid or muriatic acid (HCl) is a fixer for platinotypes. It is a gas very soluble in water, and the aqueous solution of which is known by the above names. It is obtained as a bye product in the first process of the manufacture of carbonate of soda :—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

Formerly this gas was of no use, and was allowed to escape into the atmosphere. The Alkali Acts forced the manufacturers to condense this gas, and now it is the part of their plant on which they make a profit ; such are the changes of time. Hydrochloric acid should be free from chlorine gas ; this impurity is detected by adding a drop of potassium iodide and starch solutions, when no blue colour should immediately appear. Barium chloride should give no precipitate, showing absence of sulphuric acid or sulphates.

The fixing action of this acid is by decomposing the iron oxalates, forming chlorides which are very soluble in water.

Ammonium thiosulphate ($(NH_4)_2S_2O_3$) is a body very similar to the sodium salt previously described. If used, a little potassium chlorate ($KClO_3$) should be added to the solution.

Thiosinamine ($H_2N - CS - NHC_3H_5$), or allyl-sulpho-urea, is a colourless monoclinic crystalline body, fairly soluble in water, but more so in alcohol and ether. It can be prepared from mustard oil by treating it with ammonia; or by acting on allyl-thio-carbimide with ammonia:—

$$CSNC_3H_5 + NH_3 = H_2N - CS - NHC_3H_5.$$

This substance was first recommended as a fixer by Liesegang. It dissolves silver chloride very readily, the bromide only very moderately, and the iodide practically not at all.

CHAPTER IX.

REDUCERS AND REDUCTION.

A PHOTOGRAPHER understands by a reducer a chemical which will reduce the density of a negative by attacking some of the silver deposited in the film, making a soluble compound, or a body less opaque to light than the original silver. In a chemical sense a reducing agent is a substance that will take away oxygen or the electro-negative element or group from a compound, the resultant having a less proportion of oxygen or the electro-negative element or group; if the reduction is pushed far enough, only the electro-positive element is left, chemical reduction being the exact opposite to oxidation. For example, if silver Bromide (AgBr) in a film be exposed to light and then acted on by a reducing agent, such as pyro, we get the haloid salt reduced to metallic silver, which is deposited. The pyro reduces the silver bromide and is oxidised. This reaction is identical in result with reduction of silver chloride by nascent hydrogen.

$$\underset{\text{Electro-positive element}}{\mathrm{Ag}}\;\underset{\text{Electro-negative element}}{\mathrm{Cl}} + \underset{\text{Reducer } i.e., \text{ easily oxidised}}{\mathrm{H}} = \mathrm{Ag} + \mathrm{HCl}$$

It will be obvious that when we have metallic silver deposited on a plate it is impossible, in a chemical sense, to reduce it further. If, however, we can by some means dissolve this silver and remove it from the film, or turn it into a more transparent body, we shall thereby reduce the density of the image and have a reduction in a purely photographic sense. All photographic reducers are, *ipso facto*, strong oxidisers from a chemical point of view. This must be borne in mind while reading this chapter.

Potassium ferricyanide, or red prussiate of potash ($K_3Fe(CN)_6$), is manufactured by fusing together animal refuse, crude potashes, and scrap iron, in an iron pot. The resulting mass is allowed to cool, broken up, and then extracted with water; we have now a solution of potassium ferr*o*cyanide, or yellow prussiate of potash ($K_4Fe(CN)_6$). This substance is of no use whatever for our purpose, but if chlorine gas is passed through until a portion gives no colour with ferric chloride, and the solution then evaporated down, potassium ferricyanide separates out in dark red crystals shown in fig. 11.

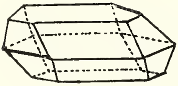


FIG. 11.—CRYSTAL OF POTASSIUM FERRICYANIDE.

Farmer's reducing solution is a mixture of potassium ferricyanide and hypo. The silver is first converted into silver ferr*o*cyanide :—

$$2Ag_2 + 4K_3Fe(CN)_6 = Ag_4Fe(CN)_6 + 3K_4Fe(CN)_6$$

This then reacts with the hypo, forming :—

$$Ag_4Fe(CN)_6 + 4Na_2S_2O_3 = 4AgNaS_2O_3 + Na_4Fe(CN)_6$$

which are soluble in water and hypo, as shown in Chapter VIII.

In order to make the difference in action between this reducer and the next one mentioned clear, let us represent the reducing action of potassium ferricyanide by means of a few diagrams. Let AB represent the section of an ordinary photographic gelatine plate exposed in a camera on a scale of four widely different tones, so that after suitable development the portion Z consists of clear glass (*i.e.*, no silver deposit), the next portion, Y, containing a small amount of silver. We will take this quantity as our unit and call it one. X will then contain twice as much, and W three times as much as Y. That is, the proportion of deposited silver in the gelatine will be Z : Y : X : W = 0 : 1 : 2 : 3.

Fig. 12.

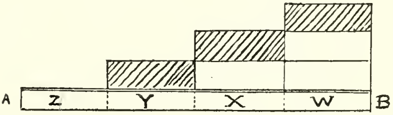


Fig. 13.

Graphically this may be represented as in fig. 13, disregarding for the present the shading.

If a solution of potassium ferricyanide and hypo be allowed to act on the above plate for a short time, say until the space Y has had all its silver removed, we shall then find that approximately an equal amount has been dissolved from the surface of X and W of the plate, that is, the shaded portions of fig. 13. The relative proportions of silver left behind will be as Z : Y : X : W = 0 : 0 : 1 : 2, which is not in the same ratio as in the first case. This is represented by fig. 14.

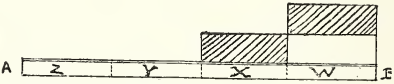
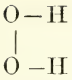


FIG. 14.

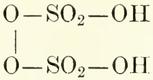
Further action would again remove the shaded portions in the latter diagram. We should then have clear glass at Z, Y, and X, but still some silver at W. This is tantamount to saying that all the details in the shadows (X, Y, Z) would have disappeared. This will be referred to again under the next chemical.

Ammonium persulphate is a white deliquescent crystalline substance formed by the electrolysis of a solution of ammonium sulphate; its formula is NH_4SO_4, or $(NH_4)_2S_2O_8$, it may be regarded as an analogue of hydrogen peroxide.



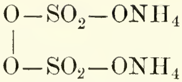
$$\begin{array}{l} O-H \\ | \\ O-H \end{array}$$

Hydrogen
peroxide



$$\begin{array}{l} O-SO_2-OH \\ | \\ O-SO_2-OH \end{array}$$

persulphuric
acid



$$\begin{array}{l} O-SO_2-ONH_4 \\ | \\ O-SO_2-ONH_4 \end{array}$$

ammonium
persulphate.

Ammonium persulphate when in aqueous solution gradually evolves oxygen, forming the sulphate, thus :—

$$(NH_4)_2S_2O_8 + H_2O = (NH_4)_2SO_4 + H_2SO_4 + O.$$

First let us see how it acts. The ammonium persulphate combines with the silver, forming a double salt of ammonium silver sulphate :—

$$(NH_4)_2S_2O_8 + Ag_2 = 2NH_4AgSO_4.$$

This is soluble in water, and is removed from the film.

We will now represent its action graphically as we did ferricyanide above.

Fig. 12 will be graphically represented as fig. 15,

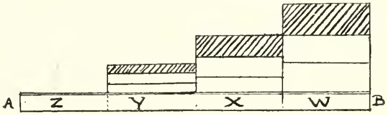


Fig. 15.

which in outline is the same as fig. 13. Accepting M. Goderus' work, the amount of silver dissolved in a certain time will be only one-third of the total deposit on any particular portion of the film.

The shaded portions of fig. 15 will be removed, the original proportion of deposit being the same as given first, namely, Z : Y : X : W = 0 : 1 : 2 : 3, but after the action, as shown graphically in fig. 15, the proportions of silver remaining will be as $0 : \frac{2}{3} : \frac{4}{3} : 2$, which is the same proportionally as in the first case (omitting, of course, the consideration of the clear glass, Z). Still further action would remove an additional third from all parts of the film proportional to the remaining deposit as represented in fig. 16; the proportions remaining, then, being $Y : X : W = \frac{4}{9} : \frac{8}{9} : \frac{4}{3}$, again the same as in the first instance.

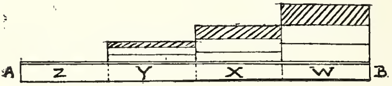


FIG. 16.

From the above it will be readily seen that the ammonium persulphate *actually* dissolves a larger amount of silver from the dense parts than from the intermediate tones, and more from these than from the thin portions. Proportionally, of course, to the amount of deposit present the solution is uniform. Surely this is selective action when compared with the older reducer.

M. Goderus, however, contests the validity of the general supposition that ammonium persulphate has a selective action; that is, it is not more active in reducing the high lights or dense parts of the negative than the shadows or thinner portions. He describes quantitative experiments (which I illustrated above) he has performed, which support his contention. These experiments, however, I think, show that there is a selective action.

To sum up, its action is in proportion to the amount of silver present at any particular place. Where there is an abundance, a large quantity is dissolved ; where there is little silver, small quantities only are removed.

The selective action is explained by Messrs. Lumière by supposing that an excess of ammonium persulphate (as, for instance, on the surface of the film) causes a deposition of silver thus :—

$$(NH_4)_2S_2O_8 + 2NH_4AgSO_4 + 2H_2O = 4NH_4HSO_4 + Ag_2 + O_2$$

This hypothesis, for that is all it amounts to, is objected to by Professor Namias, M. Helain, and others. M. Helain thinks that the selective action, or, to be more accurate, the proportional action, is due to the oxidation of the gelatine. But this lands us in the unknown domain of the chemistry of gelatine, and the natural question that would present itself would be—Why does not ferricyanide of potash also oxidise the gelatine? I think that it is a case of the well-known law of "mass reaction." There is, however, no space here to go into this very interesting subject, but simply sum it up by saying that we do not know why ammonium persulphate acts differently to potassium ferricyanide.

Eder's reducing agent is formed by adding ferric chloride (Fe_2Cl_6) to potassium oxalate ($K_2C_2O_4$), when the following takes place :—

$$Fe_2Cl_6 + 3K_2C_2O_4 = Fe_2(C_2O_4)_3 + 6KCl.$$

This solution of ferric oxalate is mixed with hypo, and the negative placed in it, when the silver forms an oxalate thus : —

$$Ag_2Fe_2(C_2O_4)_3 = Ag_2C_2O_4 + 2FeC_2O_4.$$

The silver oxalate is acted on by the hypo in a manner similar to what it does on all silver salts :—

$$Ag_2C_2O_4 + Na_2S_2O_3 = 2AgNaS_2O_3 + Na_2C_2O_4.$$

Titanic sulphate ($Ti(SO_4)_2$) is a red salt formed by dissolving titanium peroxide (TiO_3) in sulphuric acid. This reducer is supposed to act by removing the gelatine and silver.

Ceric sulphate ($Ce(SO_4)_2$—$4H_2O$) is a yellow crystalline body formed when the rare oxide of cerium is dissolved in sulphuric acid. Ceric sulphate when dissolved in water should have a drop of sulphuric acid added to it.

Potassium permanganate ($KMnO_4$) is a dark purple crystalline body consisting of rhombic prisms, which is exceedingly soluble in water, giving a beautiful dark carmine-coloured solution. This substance can be obtained by fusing manganese dioxide (MnO_2) with caustic potash (KOH) and potassium chlorate ($KClO_3$). This forms a manganate, which is converted into permanganate by passing carbonic acid gas (CO_2) through its solution. The salt is obtained on great concentration.

Iodine was discovered in seaweed ash by a French chemist named Courtois, in the year 1812. It is an opaque, blackish gray solid, forming lustrous rhombic crystals, melting at 114° and boiling at 184°. Iodine may be made by mixing some iodide, say potassium iodide, with strong sulphuric acid and manganese dioxide, and distilling off the liberated iodine. It may be purified by sublimation.

Potassium citrate.—See citrates in Chapter VII.

CHAPTER X.

INTENSIFIERS AND INTENSIFICATION.

To intensify is to increase density. This can be done by increasing the amount of deposit, or, as in the case of reducers, by altering the colour of the deposit.

Mercuric chloride, or corrosive sublimate ($HgCl_2$), is prepared by heating mercuric sulphate and common salt with a little manganese dioxide, which, however, takes no apparent part in the reaction proper :—

$$HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2.$$

The mercuric chloride can be sublimed or crystallised from water, when it forms long needles. It is a deadly poison, and should always be handled with great care, and put safely away when done with. The best antidote is white of egg, with which it forms an insoluble compound, and hence cannot be absorbed into the system.

In intensification the image is first bleached by the silver being attacked, and white mercurous chloride and silver chloride taking its place, thus :—

$$Ag_2 + 2HgCl_2 = Hg_2Cl_2 + 2AgCl.$$

To obtain the deposit black there are several methods of treatment.

First, with ammonia, which dissolves the silver chloride and forms a black ammonium dimercurous chloride :—

$$Hg_2Cl_2 + 2NH_4OH = NH_2Hg_2Cl + NH_4Cl + 2H_2O.$$

Second, with sodium sulphite, we have the mercury precipitated in the metallic form, which is blacker than the original silver which it replaces :—

$$Hg_2Cl_2 + Na_2SO_3 + H_2O = 2Hg + Na_2SO_4 + 2HCl.$$

Third, by developing with a mixture of ferrous and potassium oxalate, by which means we have the original silver redeposited, and for every atom of silver another of mercury added. It is very obvious that this considerably increases the opacity to actinic rays, and by this method the whole process can be commenced *de novo*, making the deposit still more dense.

Fourth, by treating with ammonium sulphide.

Fifth, by potassium-silver cyanide, as shown further on.

Mercuric iodide (HgI_2) is a brilliant red substance formed by the addition of a soluble iodide to a soluble mercuric salt. It must not be added to excess, otherwise the precipitate dissolves. It should be filtered, washed, and dried, when it is ready for use as recommended by Lumière.

Mercuric bromide.—A solution of this is formed by adding excess of potassium bromide to a solution of corrosive sublimate.

Schlippe's salt ($Na_3SbS_4-9H_2O$), sodium thio-antimoniate, is in the form of large yellow crystals belonging to the regular tetrahedron class. It is obtained by fusing together 13 parts of antimony sulphide (Sb_2S_3), 16 parts of anhydrous sodium sulphate, and 5 parts of charcoal, the resulting mass is dissolved in water and boiled with 2·5 parts of powdered sulphur. The liquid is filtered, then concentrated, and allowed to crystallise.

The negative is first soaked in a solution of iodine, which converts the silver into the iodide. This is then converted into a dark red compound of silver sulph-antimoniate by the action of a solution of sodium thio-antimoniate.

Uranium nitrate, uranyl nitrate ($UO_2(NO_3)_2-6H_2O$), is obtained by dissolving uranium oxide in nitric acid, when on concentration crystals of a greenish yellow colour separate out, which are very deliquescent.

Selle's uranium intensifier consists of uranyl nitrate and potassium ferricyanide. This latter substance converts the silver into a ferr*o*-cyanide, as shown in Chapter VIII. ; the other constituent then displacing the silver, forming uranium ferrocyanide, which is of a dark brown colour, and much less transparent to actinic rays than the black deposit of silver of which it has taken the place, or perhaps, to be more accurate, has combined with.

Cupric bromide ($CuBr_2$) is obtained by dissolving copper turnings in nitric acid and hydrobromic acid, or more easily by the action of potassium bromide on cupric sulphate solution, when a solution of cupric bromide is formed which is stable, and will keep for some time. Its action on metallic silver is to form silver bromide and cuprous bromide ($CuBr$), which latter on treating with silver nitrate is turned into silver bromide. After undergoing these operations the plate is exposed to light and developed as far as it will go. It will thus be seen that for every atom of silver originally present another one has been added. This process can be repeated as often as is necessary.

Potassium-silver cyanide ($AgK(CN)_2$). A suitable solution is prepared by adding silver nitrate to a 10 per cent. solution of potassium cyanide until the silver cyanide formed no longer dissolves. Filter, and the solution is ready for use. It is used for darkening the bleached image instead of ammonia or sodium sulphite.

Ammonium sulph-hydrate: many sulphides of ammonium are formed by passing sulphuretted hydrogen into ammonium hydrate, but a nearly pure solution is obtained by adding an equal quantity of ammonia after the gas has been passed through.

Yellow ammonium sulphide is a solution much used in chemical laboratories. It is prepared as in the previous case, finally adding instead of the ammonia some flowers of sulphur, which will readily dissolve, giving the yellow solution required.

CHAPTER XI

TONING CHEMICALS.

This chapter will be concerned with substances used in toning, and it would perhaps be advisable to give here a short *résumé* of the theory of toning. Put briefly, toning is the process of more or less completely substituting a metallic deposit of an undesirable colour for one more pleasing to the eye. Every one knows the colour of silver prints simply fixed in hypo. Now by substituting, say, gold or lead for various proportions of the silver, any tone can be obtained, from a brown to a blue black, which, in the latter case, means almost complete substitution. When toning takes place with gold chloride, chlorine is given off, and we must have present some body to absorb this, otherwise the process will not proceed, and for this reason we have to add other salts to the gold during toning. There are, of course, endless complications due to the various substances put into different papers by their makers, but in the main the above is what takes place.

Gold is a soft, very malleable and ductile yellow metal, but when thin sheets are viewed by transmitted light they appear of a green colour. It is found native in the metallic state, due to the fact that it is a most stable metal, and no ordinary single acid will attack it. Further, it is due to this property that it is used for toning, the image being very permanent, and moreover, its compounds are very easily reduced, making toning an easy operation.

Chloride of gold, gold trichloride, or auric chloride ($AuCl_3$), consists of reddish brown crystals ($AuCl_3-2H_2O$), very deliquescent in moist air, and efflorescent in dry air, hence always sold in sealed tubes. It is prepared by dissolving gold in aqua regia (a mixture of concentrated hydrochloric and nitric acids). The solution is then evaporated to dryness. The residue is dissolved in water, filtered, and the solution concentrated, when the gold chloride separates out in needles. Should the solution of gold be slightly acid this may be neutralised with chalk and then filtered. The gold chloride generally sold contains chloride of sodium or potassium and has the formula $AuCl_3$—$NaCl$ or $AuCl_3$—KCl.

Auric chloride is very easily decomposed, metallic gold being deposited. A little organic matter in the water will do this, hence the only safe way of keeping a solution of any gold salt is by using distilled water.

Copper sulphate ($Cu\ SO_4$—$5H_2O$) or cupric sulphate is a blue solid crystallising in the asymmetric system.

It can be prepared by dissolving copper oxide (CuO) in dilute sulphuric acid and concentrating :—

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

Lead acetate, or "sugar of lead" ($Pb(C_2H_3O_2)_2$) is sometimes used in conjunction with gold chloride for toning in combined baths. It is prepared by dissolving litharge in commercial acetic acid, evaporating down, and allowing to crystallise.

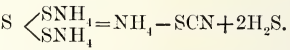
Potassium chloro-platinite has been described in Chapter VI.

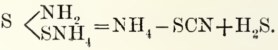
Sodium formate ($HCOONa$) is a white deliquescent salt obtained by neutralising a solution of formic acid with caustic soda and concentrating the solution until crystals are formed.

Ammonium sulpho-cyanide, or ammonium thiocyanate (NH_4SCN), is best obtained by shaking 8 parts of carbon bisulphide (CS_2) and 30 parts of concentrated ammonia, thus :—

$$4NH_4OH + CS_2 = NH_4SCN + (NH_4)_2S + 4H_2O.$$

The addition of an equal part of alcohol causes the final product to be easier obtained. The solution is evaporated down, when, on cooling, crystals separate out. Probably two substances as below are formed, which on being warmed, decompose, giving us the ammonium sulphocyanide.

Ammonium thio-carbonate,

$$CS\left\langle\begin{matrix}SNH_4\\SNH_4\end{matrix}\right. = NH_4-SCN + 2H_2S.$$

Ammonium thio-carbamate,

$$CS\left\langle\begin{matrix}NH_2\\SNH_4\end{matrix}\right. = NH_4-SCN + H_2S.$$

It may also be formed by warming a mixture of hydrocyanic acid with yellow ammonium sulphide, formed as described at end of previous chapter. The substance is in the form of white crystalline needles, which deliquesce in the air, but much less so than the potassium salt.

Potassium sulpho-cyanide, or potassium thio-cyanate ($KSCN$), is very similar in appearance and behaviour to the last compound described, but more deliquescent. It can be easily prepared by fusing together potassium cyanide, or potassium ferrocyanide with sulphur, and extracting the mass with alcohol; on concentration, crystals separate out.

NOTE.—It is perhaps needless to say that great care must be taken in the use of these two substances, as they are exceedingly poisonous, being salts of sulpho-prussic acid.

Sodium acetate ($NaC_2H_3O_2$) is a hygroscopic salt formed by neutralising caustic soda with acetic acid and crystallising in the usual way. When in this form it has three molecules of water combined with it.

Sodium phosphate.—There are many phosphates of soda, but the salt usually known under that name is the di-sodium ortho-phosphate (Na_2HPO_4). It is prepared by adding sodium carbonate to phosphoric acid until alkaline, when large transparent efflorescent monosymmetric crystals are formed (Na_2HPO_4—$12H_2O$), melting at 35°.

Common salt ($NaCl$) is sodium chloride, and is found native as rock salt, etc.

Phosphoric acids.—There are three of these—the tetra-basic or pyro-phosphoric acid ($H_4P_2O_7$), the mono-basic or meta-phosphoric acid (HPO_3), the tri-basic or ortho-phosphoric acid. This latter is the ordinary acid and is understood when no prefix is used. It is interesting to note from the above formulæ that there are eight simple phosphates of, say, potassium.

Ortho-phosphoric acid is prepared by treating bone ash (mainly calcium phosphate) with sulphuric acid,

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

filtering off the precipitated calcium sulphate, and finally evaporating down to a syrup. The pure anhydrous acid consists of deliquescent rhombic prisms which melt at 39°. The usual form found in commerce is the syrupy liquid.

Lactic acid ($C_3H_6O_3$), or oxy-propionic acid is prepared by the lactic (*lactic bacillus*) fermentation of sugar, starch, etc., at a temperature of about 35° in a neutral solution. It is only obtained as a thick, colourless, syrupy liquid.

Sodium tungstate (Na_2WO_4) is a colourless salt, fusing at a red heat.

CHAPTER XII.

ORTHOCHROMATIC CHEMICALS

All makers now claim that their own ortho- or isochromatic plates give results nearer to the correct colour value of the object photographed than any other make does. The advantages of a colour correct plate without a screen and an ordinary plate I am not going to discuss here, but only describe a few of the dyes used in the making of these plates.

By adding certain dyes to the photographic emulsion, the sensitiveness to the spectrum is increased at the red end, and decreased towards the blue. Then, by the use of a yellow or orange screen, a correct colour rendering can be obtained in monochrome.

The value of the various dyes for this class of work varies within very wide limits. Eder and Ruh of Vienna after a number of exhaustive experiments drew up the following table of relative sensitiveness taking erythrosin as the best and calling it a hundred :—

Erythrosin	100
Rose Bengal	50
Naphthofluorescein	50

Methyl-eosin		50
Ethyl-eosin		50
Eosin		25
Phloxin		25
Octoiodofluorescein		25
Cyanosin		25
Quinoline red		25
Bromnaphthofluorescein		14–16
Acridine yellow		14
Dibromnitrofluorescein		14
Chrysaniline		11–13
Monochlorfluorescein		6–7
Benzylfluorescein	(less)	6
Fluorescein	,,	6
Tetranitrofluorescein	,,	6
Nigrosin B.		1–7

Phthalophenone is the parent of most of the dyes used in orthochromatic work. It is obtained by heating phthalic chloride with benzene and aluminium chloride (Al_2Cl_6), when, on cooling colourless plates separate out, melting at 115°. By the combination of other bodies with this one the dyes are obtained, and the class is termed Phthaleins.

Fluorescein or resorcin-phthalein ($C_{20}H_{12}O_5$—H_2O) is a dark red crystalline powder soluble in alcohol with a green fluorescence. It is prepared by heating resorcin seven parts and phthalic anhydride five parts to 200° C. This substance is not of much use for orthochromatic work as will be seen from above table.

Eosin is the alkaline salt of tetra-bromo-fluorescein

($C_{20}H_6O_5Br_4X_2$) and can be obtained by adding bromine to a solution of fluorescein in acetic acid. This is the substance which red ink is made from, and if a drop of acid be added to some red ink a precipitate is formed of tetra-bromo-fluorescein. The sodium salt ($C_{20}H_6O_5Br_4Na_2$) is the "red shade eosin," and the potassium salt ($C_{20}H_6O_5Br_4K_2$) is the "yellow shade eosin."

Erythrosine, or sodium tetra-iodo-fluorescein ($C_{20}H_6I_4O_5Na_2$), is formed by the action of iodine on a solution of fluorescein.

Octo-iodo-fluorescein ($C_{20}I_8H_2O_5Na_2$) is produced from fluorescein by treatment with a very strong iodising agent.

Cyanine or Quinoline blue ($C_{28}H_{35}N_2I_2$) is the ordinary dye of commerce. It is very sensitive to the red rays when used in an emulsion, but is itself very easily decolourised by light.

Ethyl eosin is the potassium ethyl salt of tetra-bromo-fluorescein ($C_{20}H_5O_5Br_4K_2C_2H_5$).

Methyl eosin is a compound very similar to the previous one ($C_{20}H_5O_5Br_4K_2CH_3$) a methyl (CH_3) group taking the place of an ethyl (C_2H_5).

Rose Bengal. Potassium tetra-iodo-tetra-chloro-fluorescein ($C_{20}I_4Cl_4H_2O_5K_2$).

Phloxin is the potassium salt of tetra-bromo-di-chloro-fluorescein ($C_{20}Br_4Cl_2H_4O_5K_2$).

Cyanosin is the potassium methyl salt of tetra-bromo-di-chloro-fluorescein ($C_{20}Br_4Cl_2H_3K_2CH_3$).

Acridine yellow is di-amido-di-methyl-acridine hydrochlorate.

Chrysaniline is similar to the last and is a di-amido-phenyl-acridine nitrate.

Saccharoeosin is the sacchareïn compound of tetra-bromo-resorcin.

Picric acid is a yellow crystalline substance, a solution of which is sometimes used for staining screens, but not for colour sensitising films. It is a tri-nitro-phenol (1·2·4·6 $OH(NO_2)_3C_6H_2$), and can be made by the action of concentrated nitric acid on almost any organic body. Picric acid is a strong acid, slightly soluble in water but more so in alcohol, from which it can be crystallised in yellow prisms or plates melting at 122° C.

CHAPTER XIII.

MISCELLANEOUS CHEMICALS.

Alums.—There are many compounds belonging to the class of alums, but the most common is known as alum, or potassium alum ($K_2SO_4 - Al_2(SO_4)_3 - 24H_2O$). It is prepared by making a solution of potassium sulphate and aluminium sulphate in the exact proportions shown above, then concentrated and allowed to crystallise, when, if evaporation is slow, very large crystals belonging to the regular octahedron system are formed, as shown in fig. 17.

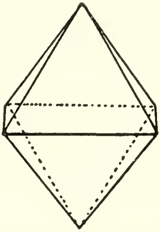
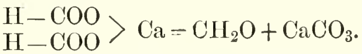


FIG. 17.—CRYSTAL OF ALUM.

Formaline, or formaldehyde (CH_2O), is the gaseous aldehyde from methyl alcohol. The formaline of commerce is a 40 per cent. solution of this gas in water. It can be prepared by heating calcium formate in a flask in the dry state, and the gas that is evolved is passed into water, and the solution thus obtained :—



$$\left.\begin{array}{l} H-COO \\ H-COO \end{array}\right> Ca = CH_2O + CaCO_3.$$

5 per cent. is the best strength for use with plates.

How alum and formaline act on the gelatine to make it insoluble is not exactly known, for the simple reason that we know nothing of the chemistry of gelatine. We have not advanced a single step in that direction during the last ten years.

Hydrofluoric acid (HF) is a gas very soluble in water. It cannot be kept in glass vessels because it attacks the silica, forming a soluble compound, and would eat through the sides in a very short time. To prepare this gas heat calcium fluoride (CaF_2) with sulphuric acid in a lead or platinum vessel :—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The solution must be preserved in gutta-percha bottles.

Boracic acid, or boric acid (H_3BO_3), is found native in lagoons in Tuscany. The water is evaporated and the acid crystallises out in shining plates very unctuous to the touch. When dilute sulphuric acid is added to a hot concentrated solution of borax, boric acid crystals separate out on cooling :—

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O = 4H_3BO_3 + Na_2SO_4.$$

Borax ($Na_2B_4O_7$), as sodium pyroborate, occurs native in Thibet as the mineral *tincal* ($Na_2B_4O_7 - 10H_2O$), and also in the borax lakes in North America. It is manufactured by neutralising boric acid with sodium carbonate when in strong hot solutions :—

$$4H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + 6H_2O + CO_2.$$

On cooling, crystals belonging to the monosymmetric system containing ten molecules of water separate out.

Oxalic acid ($H_2C_2O_4-2H_2O$) is an exceedingly poisonous white crystalline body. It may be easily prepared by boiling a solution of cane sugar with nitric acid and allowing to crystallise.

Salts of sorrel of commerce is a mixture of the hydrogen potassium salt of the previous acid (KHC_2O_4) with the acid itself. The crystals have the following formula :—($KHC_2O_4-H_2C_2O_4-2H_2O$).

Rochelle Salt is potassium sodium tartrate and crystallises in large rhombic prisms having the formula :—($KNaC_4H_4O_6-4H_2O$).

Tartaric acid ($C_2H_2(OH)_2(COOH)_2$) is found as the potassium salt in the juice of grapes. It crystallises in the monoclinic system.

Citric acid ($C_3H_4(OH)(COOH)_3$) is an acid obtained principally from lemons, but also from the fruit of other trees belonging to the citrus tribe. It crystallises with one molecule of water.

Bleaching powder or the so-called "chloride of lime" is manufactured by passing chlorine over lime :—

$$CaO + Cl_2 = Ca < \begin{matrix} OCl. \\ Cl. \end{matrix}$$

It has a peculiar odour something like chlorine, and is used as a bleacher.

Glacial acetic acid ($C_2H_4O_2$) or constitutionally (CH_3-COOH). This acid is manufactured on a large scale by the dry distillation of wood. The brown aqueous distillate obtained is again distilled with lime; calcium acetate being left in the retort as a concentrated solution, this is skimmed and hydrochloric acid added and again distilled, when a dilute acetic acid solution is obtained and is put on the market as commercial acetic acid. To obtain the anhydrous or glacial acid, anhydrous sodium acetate is distilled with concentrated sulphuric acid, and a distillate is obtained which crystallises on cooling to a hygroscopic colourless solid.

Alcohol, or spirits of wine (C_2H_5-OH), can be obtained in the following manner. A solution of cane sugar is made and brewer's yeast added, and the whole kept warm until fermentation ceases. The solution is now filtered and distilled, the distillate is mixed with lime and again distilled, when fairly pure ethyl or ordinary alcohol is obtained.

Methylated spirit is ordinary alcohol mixed with 10 per cent. of partially purified wood spirit, and a very small quantity of paraffin-oil. Alcohol, when it has undergone this process is obtained duty free, as it is then supposed to be undrinkable, but will still answer for most other purposes.

Ether or Æther is the name given to a number of compounds consisting of oxides of organic radicles. Under the above name ethyl ether or ethyl oxide is known. It is a volatile liquid obtained by heating alcohol with sulphuric acid. The acid acts as a dehydrating agent, taking water out of the alcohol, leaving commercial ether which distils over :—

$$\begin{array}{c} C_2N_5OH \\ + \\ C_2H_5OH \\ \textit{alcohol} \end{array} = H_2O + \begin{array}{c} C_2H_5 \\ C_2H_5 \!>\! O \\ \\ \textit{ethyl ether.} \end{array}$$

Starch $(C_6H_{10}O_5)_n$ is a white powder obtained from tubers and seeds, mainly rice, potatoes, Indian corn, arrowroot, etc. It can be obtained very easily from flour by tying up a quantity of it in a muslin bag and washing the starch out, leaving the glutin behind. On allowing the wash water to stand, starch settles to the bottom.

Chemically, starch is a mixture of two substances. The grains consist of an outer layer impervious to water, and an inner portion which escapes when the grain is heated or boiled in water. A weak solution of iodine gives with a small quantity of boiled starch a beautiful blue colour which disappears on heating, returning, however, on cooling.

Dextrin, or " British gum," is obtained by heating starch to 200°C. Its formula is the same as starch, the value of n being different. It is soluble in water, and does not give a blue colour with iodine.

Glycerine, or Glycerol $(C_3H_5(OH)_3)$, is obtained as a bye-product in soap manufacture, by the saponification of natural fats and oils, which consists of the glycerol compounds of stearic, palmitic, and oleic acids. It is a sweet, colourless, oily liquid.

Microcosmic salt ($HNa(NH_4)PO_4$) is a salt used in blowpipe analysis.

Gelatine.—Very little indeed is known of the chemistry of this substance. It consists of two bodies :—

(*a*) Gluten $(C_{16}H_{25}N_5O_6)_n$, which is the more soluble and is not precipitated by alum.

(*b*) Chondrin $(C_{16}H_{25}N_4O_7)_m$, which is precipitated by alum.

Albumen is the name given to some natural bodies which contain sulphur in addition to what gelatine contains.

Collodion is a solution of nitrocellulose containing a low percentage of nitrogen generally in a mixture of one part alcohol and three parts ether.

Gums are amorphous carbohydrates $(C_6H_{10}O_5)_n$, which swell up enormously when placed in water, and give on dissolving a very thick solution.

APPENDIX I.

ATOMIC AND MOLECULAR WEIGHTS OF THE MORE IMPORTANT ELEMENTS, TOGETHER WITH THEIR SYMBOLS.

ELEMENT.	ATOMIC WEIGHT.	MOLECULAR WEIGHT.	SYMBOL.
Hydrogen	1	2	H.
Helium	4	4	He.
Lithium	7	—	Li.
Boron	11	—	B
Carbon	12	—	C.
Nitrogen	14	28	N.
Oxygen	16	32	O.
Fluorine	19	—	F.
Sodium	23	—	Na.
Magnesium	24·4	—	Mg.
Aluminium	27·1	—	Al.
Silicon	28·4	—	Si.
Phosphorus	31	124	P.
Sulphur	32	64	S.
Chlorine	35·5	71	Cl.
Potassium	39·2	—	K.
Argon	39·9	39·9	A.
Calcium	40·1	—	Ca.
Titanium	48·1	—	Ti
Chromium	52·1	—	Cr.
Manganese	55	—	Mn.
Iron	55·9	—	Fe.
Nickel	58·7	—	Ni.
Cobalt	59	—	Co.
Copper	63·6	—	Cu.
Zinc	65·4	—	Zn.
Arsenic	75	300	As.
Selenium	79·2	—	Se.
Bromine	80	160	Br.
Strontium	87·6	—	Sr.
Molybdenum	96	—	Mo.
Silver	108	—	Ag.
Cadmium	112·4	—	Cd.
Tin	119	—	Sn.
Antimony	120·2	—	Sb.
Iodine	126·8	253·6	I.
Barium	137·4	—	Ba.
Cerium	140	—	Ce.
Tungsten	184	—	W.
Platinum	194·8	—	Pt.
Gold	197·2	—	Au.
Mercury	200	—	Hg.
Lead	206·9	—	Pb.
Bismuth	208·5	—	Bi.
Radium	225	—	Ra.
Uranium	238·5	—	U.

APPENDIX II.

WEIGHTS AND MEASURES.

1. English.

Avoirdupois Weight.

437·5 grains (grs.) ... ... = 1 ounce (oz.)
16 ounces * ... ... = 1 pound (lb.)
14 pounds ... ... = 1 stone (st.)
2 stones ... ... = 1 quarter (qr.)
4 quarters ... ... = 1 hundredweight (cwt.)
20 hundredweight ... ... = 1 ton

Long Measure.

12 inches (ins.) ... ... = 1 foot (ft.)
3 feet ... ... = 1 yard (yd.)
220 yards ... ... = 1 furlong
8 furlongs ... ... = 1 mile

Liquid Measure (volume).

60 minims ... ... = 1 fluid drachm (drm.)
8 drachms ... ... = 1 ,, ounce (fl. oz.)
20 ounces † ... ... = 1 pint
2 pints ... ... = 1 quart (qt.)
4 quarts ... ... = 1 gallon

2. Metric.

Weight.

10 milligrammes ... ... = 1 centigramme
10 centigrammes ... ... = 1 decigramme
10 decigrammes ... ... = 1 gramme
10 grammes ... ... = 1 decagramme
10 decagrammes ... ... = 1 hectogramme
10 hectogrammes ... ... = 1 kilogramme

---

* 16 drams are equal to 1 oz. ; therefore 1 drm. = 27·344 grains.

† 4 gills = 1 pint, but in certain parts of England the gill is called a noggin, and there 2 noggins = 1 gill, and 2 gills = 1 pint.

Length.

10 millimetres ... ... = 1 centimetre
10 centimetres ... ... = 1 decimetre
10 decimetres ... ... = 1 metre
10 metres ... ... = 1 decametre
10 decametres ... ... = 1 hectometre
10 hectometres ... ... = 1 kilometre

Liquid.

10 millilitres [*] ... ... = 1 centilitre
10 centilitres ... ... = 1 decilitre
10 decilitres ... ... = 1 litre
10 litres ... ... = 1 decalitre
10 decalitres ... ... = 1 hectolitre
10 hectolitres ... ... = 1 kilolitre

---

[*] A millilitre is generally called a cubic centimetre (c.c.).

APPENDIX III.

MELTING AND BOILING POINTS.

(*All degrees in Centigrade scale.*)

SUBSTANCE.	MELTING POINT.	BOILING POINT.
Acetic acid	16	117
Alcohol absolute	—	78
Amidol	decomposes	—
Bees wax	62-70	—
Benzene	6	80·4
Boric acid	186	—
Bromine	—22	60
Carbon bisulphide	—	47
Citric acid	100	—
Common salt	772	—
Cupric chloride	498	—
Cuprous chloride	434	—
Diphenal	148	—
Eikonogen	decomposes	—
Ether	—	35
Glass	1,200	—
Glass (lead)	1,000	—
Glycerine	—	290
Gold	1,075	—
Hydroquinone	169	sublimes
Iodine	113	sublimes
Lead	326	—
Lead chloride	498	—
Magnesium	500	—
Metol	decomposes	—
Mercury	—39	357
Mercury chloride	293	—
Ortol	decomposes	—
Para-amido-phenol	decomposes	—
Paraffin	45—65	above 300
Phenol	40	183
Phosphorus	44	269
Potassium carbonate	834	—
Potassium iodide	634	—
Pyro	130	sublimes 210
Pyrocatechin	102	242
Resorcine	112	274
Silver	960	—
Silver chloride	451	—
Silver nitrate	217	—
Sodium carbonate	814	—
Sulphur	115	440
Sulphuric acid	—	338
Tri-amido-phenol	decomposes	—
Wax, Bees	62—70	—
Wax, Paraffin	45—65	over 300

APPENDIX IV.

COMMON CHEMICAL NAMES AND THEIR PROPER NAMES.

Alabaster	Calcium sulphate
Alum	See page 95
Aqua fortis	Nitric acid
Aqua pura	Pure water
Aqua regia	Mixture $1HNO_3$ & $3HCl$.
Asbestos	Magnesium silicate
Benzole	Benzene
Blue stone	Copper sulphate
Blue vitriol	,, ,,
Calc spar	Calcium carbonate
Calomel	Mercurous chloride
Carbolic acid	Phenol
Caustic potash	Potassium hydrate
Caustic soda	Sodium hydrate
Chalk	Calcium carbonate
Common salt	Sodium chloride
Copperas	Ferrous sulphate
Corrosive sublimate	Mercuric chloride
Corundum	Aluminium oxide
Cream of tartar	Potassium bitartrate
Dolomite	Magnesium and calcium carbonate
Emery	Impure corundum
Epsom salts	Magnesium sulphate
Formalin	Solution of formaldehyde
French chalk	Magnesium silicate
Galena	Native lead sulphide
Glauber's salt	Sodium sulphate
Glucose	Grape sugar

Goulard water	Solution of basic acetate of lead
Green vitriol	Ferrous sulphate
Gypsum	Calcium sulphate
Heavy spar	Barium sulphate
Horn silver	Native silver chloride
Iceland spar	Crystallised calcium carbonate.
Iron pyrites	Iron sulphide
Jeweller’s putty	Stannous oxide
Lime	Calcium oxide
Litharge	Oxide of lead
Lunar caustic	Impure silver nitrate
Marble	Calcium carbonate
Microcosmic salt	Sodium ammonium phosphate
Mosaic gold	Bi-sulphide of zinc
Muriatic acid	Hydrochloric acid
Oil of vitriol	Sulphuric acid
Plaster of Paris	Calcium sulphate
Pyrites	Natural metallic sulphides
Quartz	Silica
Quicklime	Calcium oxide
Realgar	Arsenic sulphide
Red lead	Lead oxide
Red prussiate of potash	Potassium ferricyanide
Rochelle salt	Potassium sodium tartrate
Rock-salt	Sodium chloride
Rust	Iron oxide
Sal ammoniac	Ammonium chloride
Sal volatile	Dilute ammonium hydrate
Saltpetre	Potassium nitrate
Salts of lemon	Salt of oxalic acid
Salts of sorrel	Potassium salt of oxalic acid
Salts of tartar	Potassium carbonate
Schlippe’s salt	See page 84
Slacked lime	Calcium hydrate
Soap stone	Talc

Soda	Sodium carbonate
Spirits of hartshorn	Solution of ammonia
Spirits of salts	Hydrochloric acid
Stucco	Calcium sulphate
Sugar of lead	Lead acetate
Sylvine	Potassium chloride
Talc	Magnesium silicate
Tartar emetic	Potassium antimony tartrate
Tincal	Native borax
Verdigris	Basic acetate of copper
Vermilion	Sulphide of mercury
Vinegar	Often coloured dilute acetic acid
Volatile alkali	Ammonia
White vitriol	Zinc sulphate
Wollastonite	Calcium silicate
Yellow prussiate of potash	Potassium ferrocyanide

APPENDIX V.

KEEPING QUALITIES OF PHOTOGRAPHIC CHEMICALS.

In this table only approximate keeping qualities are given, as by additions, some solutions will keep a long time, which without the addition would not remain good for a day. For example, pyro alone would only keep an hour or so, but with sodium sulphite or nitric acid it will keep for weeks.

(D.B. = dark-coloured bottles, and in every other case well corked or stoppered bottles.)

CHEMICAL.	SOLID.	SOLUTION.
Acetone (liquid)	—	Indefinitely
Alum	Indefinitely	,,
Amidol	D.B. A year or so	A few hours
Ammonium hydrate ...	—	Indefinitely
,, bromide ...	Indefinitely	,,
,, sulphocyanide	,,	A few months
Auric chloride	,,	Indefinitely
Benzene (liquid)	—	,,
Borax	Indefinitely	,,
Bromine	,,	A few weeks
Citric acid	,,	Indefinitely
Diphenal	—	D.B. Months
Eikonogen	D.B. A year or so	A few days
Ferric oxalate	A few months	,, weeks
,, chloride	Indefinitely	Indefinitely
Ferrous oxalate	A few weeks	D.B. A few days
,, sulphate	Indefinitely	,, weeks
Formaline (gas)	—	,, months
Glycin	Indefinitely	D.B. ,, weeks
Gold chloride	,,	indefinitely

CHEMICAL.	SOLID.	SOLUTION.
Hypo	Indefinitely	Long time, according to strength
Hydrochloric acid (gas)	—	Indefinitely
Hydroquinone	D.B. Indefinitely	A few weeks
Iodine	Indefinitely	D.B. A few months
Lead acetate	A year or so	A year or so
Metol	D.B. A year or so	A few days
Mercuric chloride	Indefinitely	Indefinitely
,, iodide	D.B. ,,	—
Nitric acid	—	Indefinitely
Ortol	D.B. A year or so	—
Oxalic acid	Indefinitely	Indefinitely
Para-amido-phenol	D.B. Indefinitely	An hour
Potassium bichromate	Indefinitely	Indefinitely
,, bromide	,,	,,
,, carbonate	,,	,,
,, chloro-platinite	,,	,,
,, ferricyanide	,,	D.B. A few days
,, permanganate	,,	,, ,,
,, sulpho-cyanide	,,	,, months
Pyro	D.B. A year or so	,, hours
Pyrocatechin	D.B. ,, ,,	,, days
Silver nitrate	D.B. Indefinitely	D.B. Indefinitely
Sodium acetate	,,	,,
,, bicarbonate	Indefinitely	,,
,, carbonate	,,	,,
,, sulphite	,,	A few days see page 113
,, phosphate	,,	Indefinitely
Sulphurous acid (gas)	—	A week or so
Tri-amido-phenol	D.B. A few weeks	D.B. A few weeks
Uranium nitrate	Indefinitely	Indefinitely

APPENDIX VI.

RECOVERY OF SILVER FROM WASTE LIQUORS.

Most of the silver a photographer throws away is in his hypo baths, and it is from this that the greatest difficulty is met with in recovering it. I will describe briefly how this can be done in the several cases.

All solutions containing silver, but no hypo, should be thrown from time to time into a large jar with a small quantity of common salt, and when full, the clear supernatent liquid is poured away, leaving the precipitated silver chloride at the bottom of the vessel, then proceed to add silver waste solutions and salt as before, until a fair quantity of crude silver chloride has been collected. The silver residue may now be treated in one of two ways, of which I recommend the second.

1. Wash thoroughly the precipitated silver chloride and boil gently for an hour or more with caustic soda, adding from time to time a small quantity of glucose. Filter from the dark brown liquid and wash the residue thoroughly, it will be found to differ little in appearance from the original silver chloride. It is now, however, finely divided metallic silver, which may be melted into a button of the metal, by fusing with a blowpipe flame on a bone ash cupel. The silver may now be converted into the nitrate as described on page 38.

2. Send the crude silver chloride to the most convenient silver refiner who will allow full value for it.

The hypo solutions containing silver must be treated in an entirely different way and the process is much more difficult. Collect the solutions in a large jar until nearly full; then add some sodium sulphide or liver of sulphur solution and stir vigorously for a time, allow to settle for a day or so, then agitate again and repeat two or three times. Pour off the clear liquid and put the residue into a smaller jar, then proceed as before until a fair quantity of silver sulphide is obtained. It can now be reduced to metallic silver by fusing with a mixture of sodium carbonate and potassium nitrate. This is a much more difficult process than in the preceding case and I recommend the sale of the crude sulphide of silver.

APPENDIX VII.

USEFUL FACTORS.

To convert	kilometres to miles	×	0·6214
,, ,,	metres to feet	×	3·2809
,, ,,	centimetres to inches	×	0·3937
,, ,,	sq. metres to sq. yards	×	1·196
,, ,,	miles to kilometres	×	1·6093
,, ,,	feet to metres	×	0·3048
,, ,,	inches to metres	×	0·0254
,, ,,	,, centimetres	×	2·54
,, ,,	sq. yards to sq. metres	×	0·8361
,, ,,	miles to feet	×	5280·0
,, ,,	feet to miles	×	0·000189
,, ,,	sq. feet to sq. inches	×	144·0
,, ,,	sq. inches to sq. feet	×	0·006944
,, ,,	litres to cubic feet	×	0·03532
,, ,,	,, gallons	×	0·22
,, ,,	c.c. to oz.	×	0.035
,, ,,	,, drams	×	0·0044
,, ,,	oz. to c.c.	×	28·400
,, ,,	drams to c.c.	×	3·55
,, ,,	cubic feet to litres	×	28·33
,, ,,	,, inches to cubic feet	×	0·00058
,, ,,	,, ,, gallons	×	0·003607
,, ,,	gallons to cubic feet	×	0·16037
,, ,,	,, litres	×	4·543
,, ,,	pints to cubic centimetres	×	567·936
,, ,,	cubic feet to gallons	×	6·235
,, ,,	kilogrammes to pounds	×	2·2046
,, ,,	grammes to grains	×	15·432
,, ,,	pounds to kilogrammes	×	0·4535
,, ,,	grains to grammes	×	0·0648
,, ,,	ounces to ,,	×	28·349
,, ,,	grammes per litre to grains per gallon	×	70·0
,, ,,	parts per 100,000 into grains per gallons	×	0·7
,, ,,	grains per gallon to grammes per litre	×	0·014286

To convert degrees C. to degrees F. × 1·8 and + 32

" " " F. " C. — 32 then × 5 ÷ 9

Density = weight of 1 cubic centimetre of the substance

Volume of a gas varies directly as the temperature

" " " indirectly as the pressure

$\pi = 3\cdot1416$.

APPENDIX VIII.

KEEPING QUALITIES OF SODIUM SULPHITE SOLUTION.

DURING the early part of last year the author performed a series of experiments on the decomposition of sodium sulphite when in solutions of various strengths.

One series was done in the dark and another alongside in the daylight; no practical difference was observed between these two. The experiments were repeated at intervals of about three months. Although the rate of decomposition from sulphite to sulphate ($Na_2SO_3 + O = Na_2SO_4$) varied in a marked degree, it was quite possible to draw out an average curve, a table from which I give below. To show how care in preparing solutions will affect the result is typified by a recent experiment. A twenty per cent. solution of crystallised sodium sulphite was made up with distilled water which had been previously thoroughly boiled. After standing in a half empty well-corked bottle for ten days, it was found to have lost less than one per cent.

The following table will give an idea of the approximate strength of a sulphite solution after standing a number of days in a bottle somewhere about half full. The fuller the bottle the slower will be the decomposition and *vice versa*.

Days standing.	Five per cent. solution.	Ten per cent. solution.	Twenty per cent. solution.
One	3·5	8·8	19·0
Two	2·5	7·4	18·2
Three	1·8	6·0	16·8
Four	1·1	4·6	15·6
Six	·5	3·2	14·4
Eight	·0	1·4	13·2
Ten	·0	·4	11·5
Twelve	·0	·0	8·5
Fourteen	·0	·0	6·0
Sixteen	·0	·0	5·0

N.B.—Per cent of crystalline sodium sulphite.

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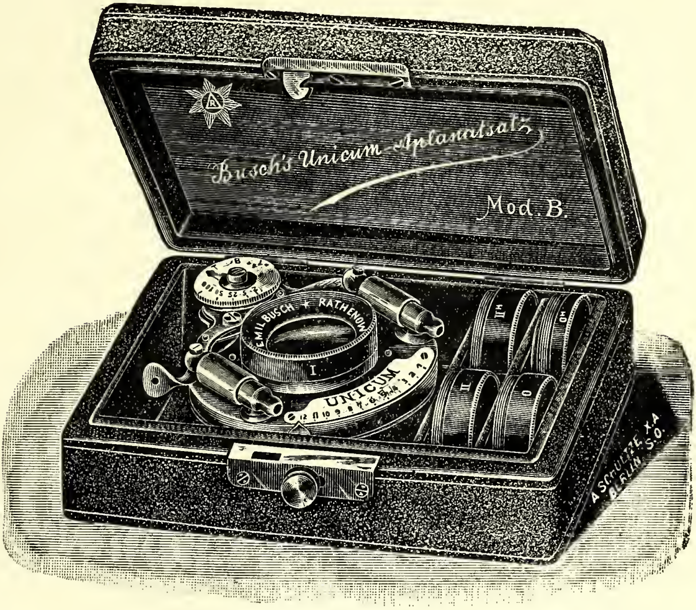

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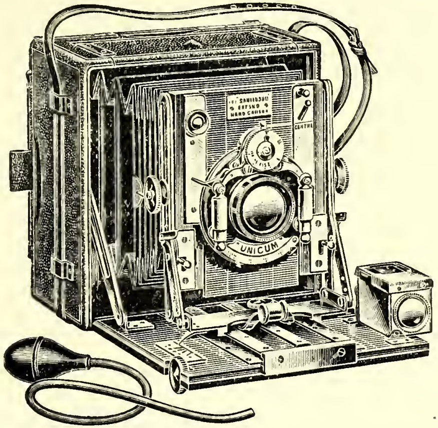
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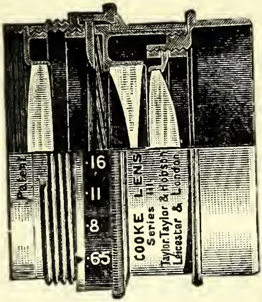

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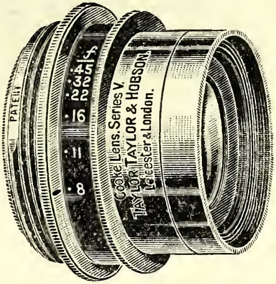

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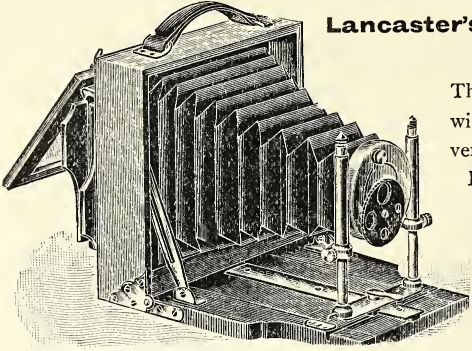

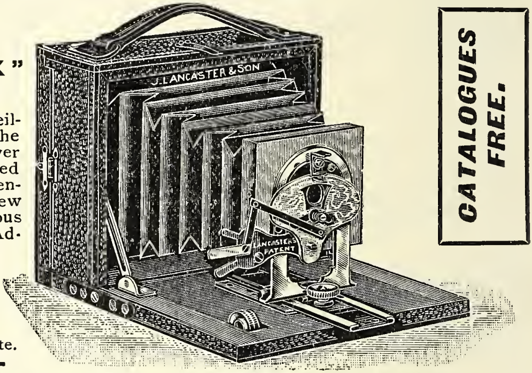
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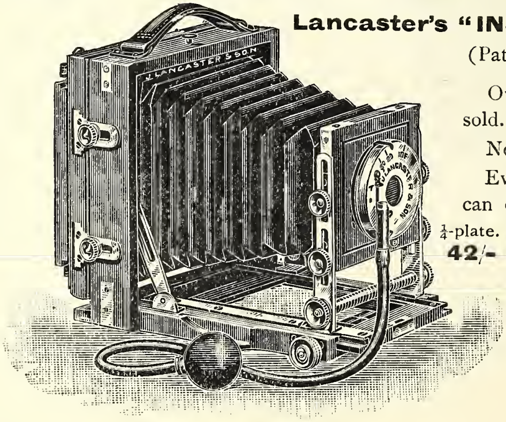
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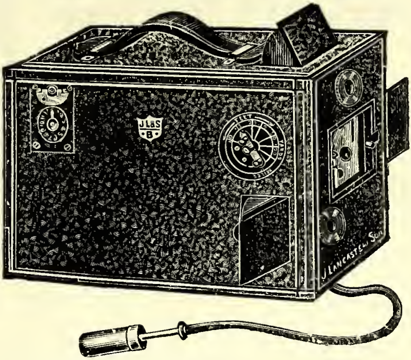
J. LANCASTER & SON, Opticians, Birmingham.

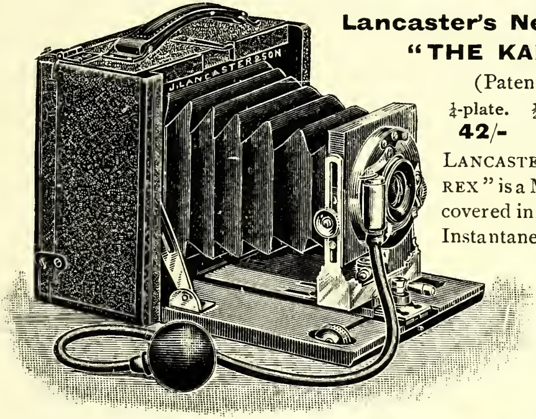
The **L** OMNIGRAPH carries twelve films or plates; has Finder, Rack-work Adjustment, and Iris Diaphragm; the Camera is covered in leather.

¼-plate.	5 × 4	½-plate.
31/6	**45/-**	**63/-**

The **R L** OMNIGRAPH has Rectilinear Lens, with "Iris" shutter for Time or Instantaneous, and carries twelve films or plates.

¼-plate.	5 × 4	½-plate.
42/-	**63/-**	**84/-**





Lancaster's New Camera, "THE KAMREX"

(Patent).

¼-plate.	½-plate.	1/1 plate.
42/-	**84/-**	**126/-**

LANCASTER'S NEW "KAMREX" is a Mahogany Camera, covered in best Leather, with Instantaneous Lens and Shutter, new Rack Front Stage, Double Dry Slide, and Stand.

Lancaster's "STOPIT."

No. 1.—Carrying six ¼-plates, **10/6**

No. 2.—Ditto, with Rack Adjustment, **15/-**

No. 3.—Ditto, ditto, carrying twelve plates, **21/-**

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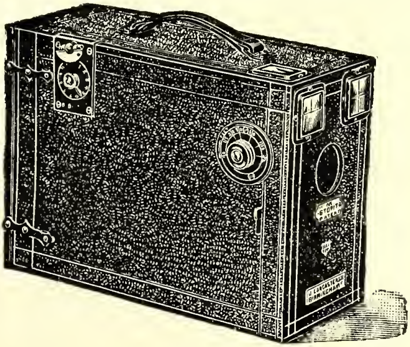
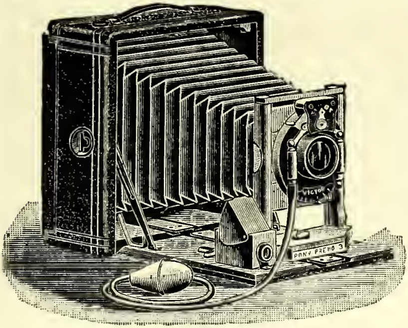




PONY PREMO

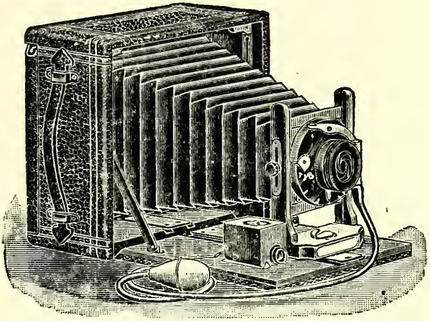
No. 3.

This Camera has reversing back, rising and falling front, also swing back, fitted with B. and L. Victor shutter and Rapid Rectilinear lens, brilliant view finder, T. level, covered with seal grain leather.

	4 × 5
Price, in case, with three holders	**£3 15 0**
Extra holders	**0 4 0**

RAY CYCLE

No. 1.—Style 2.

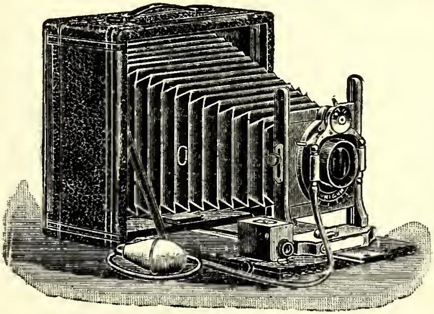


This Camera is highly finished and fitted with B. and L. Gem shutter, and selected RR lens.

Price, complete in case, with one holder—

4 × 5	½-plate.
£2 2 0	**£3 3 0**

Extra holders, **4/3** and **5/6**



RAY CYCLE

No. 9.

This Camera has reversing back, rising front, rack and pinion, fitted with Auto shutter, and symmetrical lens in the 5 × 4 and ½ size.

Price, complete in case, with one holder—

¼-plate. RR	4 × 5 RS	½-plate. RS
£3 10 0	**£4 4 0**	**£5 12 6**

Extra holders, **4/3**, **4/3**, and **5/6**

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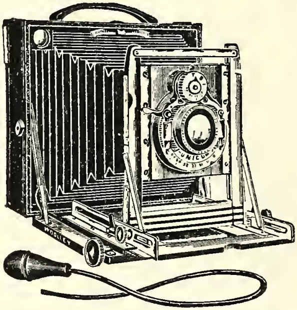
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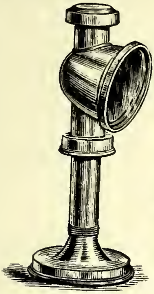

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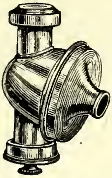

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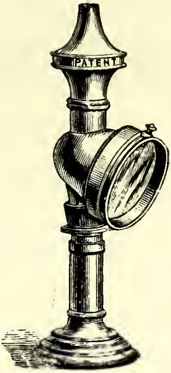
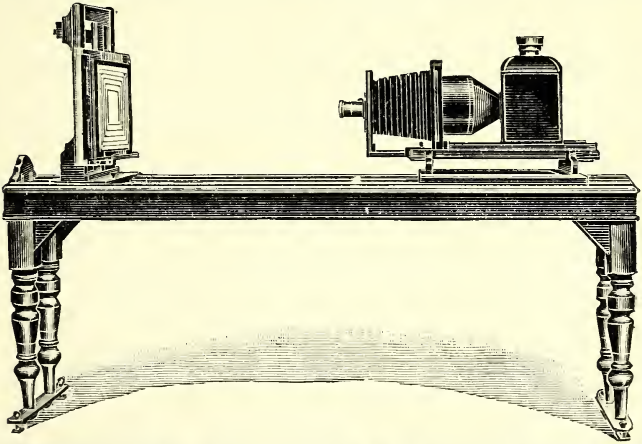
TRAVELLING.



PERFECTION
LAMP.



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