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THEIR PREPARATION AND COATING ON GLASS, CELLULOID AND PAPER, EXPERIMENTALLY AND ON THE LARGE SCALE

BY

E. J. WALL, HON. F.R.P.S., F.C.S.

Author of "The Dictionary of Photography,"
"The History of Three-Color Photography,"
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OMNIA POSSIBILIA VOLENTI

BOSTON
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COOPER

James B. Cooper

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PREFACE

EMULSION making is not a subject of absorbing interest to the average photographer who is content to purchase a few plates or rolls of film for making pictures or records. On the other hand there are a few misguided enthusiasts who hope that they can make as good sensitive materials as are obtainable commercially, and at a much lower cost. To such this little treatise may appeal. But the author would most strongly emphasize the point that if anyone supposes that it is possible to learn emulsion making by mere reading of a few printed pages, or to turn out sensitive products with regular characteristics at a cost that will make a considerable saving, he is considerably mistaken. This idea is purely chimerical.

As a field for experiment, emulsion making is extremely fascinating. As a means of spending money it is only equalled by dabbling in stocks. In both cases one has the excitement of waiting for results, which may be all that one desires or merely a loss of time and money.

One point must be recognized once for all, that to expect to turn out good results in a darkroom that has been used for the ordinary operations of development and fixing is utterly hopeless. Perfect cleanliness and freedom from chemical dirt is a *sine qua non*. The average darkroom is, from the chemical point of view, more likely to be extremely dirty than clean, in consequence of traces of the developing and fixing agents being present on the benches and floor. This chemical dirt, finding its way into the emulsion or on to the surface of the coated material while drying, will at once give rise to a host of troubles. The novice will find that there are quite enough pitfalls without these additional ones being provided. It is almost impossible to rid a room of such matter when it has once been spilt on the floor and benches, and more or less disseminated in the shape of dust.

If any excuse is needed for the publication of this work, it may possibly be found in the fact that since Abney's "Photography with Emulsions (1885)," Eder's "Photographie mit Bromsilber-Gelatine und Chlorsilber-Gelatine (1903)," and the writer's translation of an earlier edition of this latter work, which appeared serially in a photographic journal in 1892, there has been no work available on the subject.

The information given is based on many years' practical experience, but even so it is not possible to indicate all those little points which can only be learnt by continued experiment, and which may be called "tricks of the trade," though no attempt has been made to withhold any information. On the other hand no trade secrets have been disclosed nor any confidences violated, even if such be in the writer's possession.

The main purpose of the book is to point out the lines on which work may be undertaken with a reasonable chance of success: to fill, if possible, the gap expressed in the following quotation and render it unnecessary to carry out such an extended number of experiments: " There is nothing in the literature upon the subject (photographic emulsions) which helps one much when undertaking this sort of research work. Practically all the knowledge is secreted in the great factories. The worker at this point stands practically in the position of the man who first discovered emulsion photography, and he must battle his way through and pull himself up until he has acquired a knowledge equal to what is known at the present day. This is far from a simple matter, but once I set to the task it proved tremendously fascinating. In order to have as few variables as possible, I purchased an enormous roll of paper and a large quantity of gelatine and set to work. In the first four years of this research work, over three thousand very carefully arranged and recorded emulsions were made and approximately five miles of paper, thirty inches in width, was used. Energy was poured in ruthlessly — Sundays, holidays and nights, frequently until one and two o'clock in the morning." This statement was made in 1925.

Historical data have been purposely omitted, for while extremely interesting to some, they are not necessary for learning the rudiments of emulsion making.

Successful emulsion making depends upon so many and in some cases such apparently trivial factors that the information given must be looked upon rather as signposts pointing the way than milestones conveying definite and accurate information, though no formula or method is given that has not been tried out practically.

Finally it should be pointed out that if the subject is to be seriously tackled, the mere coating and exposure of a few plates and bits of paper will lead nowhere. Accurate testing methods by the sector wheel or neutral wedge, with photometric readings of both plates and papers, are essential. Only if this be done and one single factor be varied in the next experiment, can one hope to learn the real bases of the work, and attain that position from which one can speak, with some definite hope of being correct, of the possible sources of failure or success.

Occasional references will be found to notes, which are collected at the end of each chapter.

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CHAPTER I

THE WORKROOM: FITTING AND ROUTINE

POSSIBLY a few notes or suggestions as to the fitting up of an emulsion room, etc., may not be out of place.

First, as regards the mixing room, experience has proved that the best material for the floor is concrete, properly treated so that it will not powder up, though this need not be much feared, as there is too much water used in the room for this to cause trouble. The floor should slope to a central drain. Wooden grid stands should be made to cover the whole floor, raised about two inches by cleats underneath. These grids should not be more than six or eight feet long and three or four feet wide, so that they can be easily handled by one man, and lifted and stacked against the wall, when the room is cleaned.

The walls should preferably be plaster-faced, well smoothed, thoroughly dried and then painted liberally with three coats of good white oil-paint, and the ceiling should be treated in the same way. The purpose of this is to prevent damage from condensation of moisture. The mixing tanks should be provided with a hood, as in a chemical laboratory fume cupboard, and a good exhaust fan should be provided to draw off any steam or ammonia fumes that may be set free in digestion.

As regards the tanks for containing the mixing crocks, these will naturally be made for a given number, three or six as the case may be, and it will be found that rectangular tanks of cypress wood are more satisfactory than metal. The internal measurements of the tanks will depend on the size of the crocks. Three inches clear should be allowed round each pot on all sides, and the depth should be the same as that of the pot.

Each tank should be provided with a good-sized outlet pipe at the bottom, so that it can be emptied; an inch or inch and a half pipe, with quick screw-down valve, should be used. Over each tank should be an inch supply pipe for cold water. At the bottom of each tank should be a coil of piping for bringing live steam into the tank. This coil should, preferably, be copper, one half inch in diameter, with not less than six turns in a tank about two feet wide. The coil may end in an open pipe, but this is not so convenient as a closed coil, which carries the steam right through.

If a long period of digestion is adopted, such as eight to ten hours, a thermo-regulator should be fitted to control the steam supply. This may seem a refinement, but it is a good safeguard against steam leakage and consequent rise in temperature, and there is no steam valve yet made which will not leak in time.

When live steam is not available, gas must be used. In this case the tanks must be made of copper, and a flue with good draft arranged to carry off the burnt gas products. Gas is certainly not so convenient as steam. If the metal tanks are used, then the front and the top front edge should be covered with wood, as this prevents the operator from accidentally touching the hot metal. Naturally the gas burner must be entirely enclosed, so as to prevent egress of light into the room.

In both cases the bottoms of the tanks should be provided with light wooden grids to prevent the crocks from resting on the steam pipes, or the bottom of the tank when gas is used for heating, thus preventing local heating of a crock. Every tank should have an overflow pipe, not less than two inches in diameter, which will carry off the water when it rises above a certain height. The height of the tanks from the floor should be just so that a workman can conveniently lift a pot out, without having to raise it much above his waist.

There are two little suggestions that will be found great conveniences to the mixer. One is to provide a narrow shelf at the side or preferably at the back of the tank; this need not be more than three inches wide and should have a marked slope towards the wall. This comes in handy for the reception of a thermometer or a pocket flash lamp. A larger flash lamp with one or two thicknesses of stained papers inside the lens, or the plane side of the lens coated with non-actinic gelatine, is a great convenience, though this may be dispensed with if a safelight, which can be switched on and off, is arranged over the tank.

Another thing that will be found an advantage is to have silver guards made for the thermometers, as shown in Fig. 1. These will be found to pay for themselves in a very short time in saving breakage of thermometers, especially if a mechanical stirrer be fitted. The following are the dimensions of a silver guard that the writer has had in use for over twenty years, during which time only two thermometers have been broken. In both cases it was by an accidental drop on the floor, and not in the emulsion crock. The total length *AB* is 28 cm, the internal diameter 1.25 cm, and the thickness of the metal 1.2 mm. The length from *A* to *C* is 4 cm, from *C* to *D*, 16 cm, from *D* to *B*, 8 cm. Between *D* and *B* are punched three rows of three holes each, the diameters of these being 3 mm. The end at *B* is plugged with a piece of cork, against which the bulb of the thermometer rests, another piece of cork at *A* keeping the tube firm. At the end is a brass ring, three quarters of an inch in diameter, which serves to hang the whole up on a nail. On the side of the tube from *C* to *D* a small section of the wall is cut out, the width of this cut-out piece being 10 mm, and through this the height of the mercury is read.

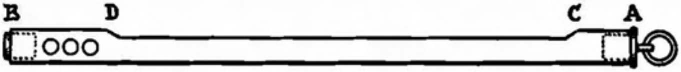

FIG. 1

The most satisfactory thermometers are those made on the principle of the ordinary clinical thermometers, that is, with a broken thread of mercury, so that the temperature can be read without having to stoop over the crock for fear the mercury should sink as the thermometer is removed from the emulsion.

It is possible also to obtain thermometers with an alcohol column, instead of the mercury, and if this be stained with toluidin blue, or a green dye, which looks black by red light, it is much easier to read.

Little need be said about the general illumination of the room; but the indirect lighting system is the most satisfactory. A separate white light fixture should be provided, but this should be controlled by a key switch, and the key should be in the possession of the foreman only, so that white light cannot be accidentally turned on. The idea in providing white light is for cleaning purposes, and the writer always devoted Saturday morning to this unpleasant but necessary job. Then all mixing was suspended; the white light was switched on, the floor grids lifted against the walls and the hose turned on them. All the tanks were emptied and a stiff broom used in each, while the water was running out, so that the dirt, which is usually in the form of splashes of emulsion, was swept out by the water. The water should be brushed down to the drain and a hose turned on the floor, and there should be a generous supply of hot and cold water behind the hose, taken from a convenient tap in the wall. This tap should be by the side of one of the tanks, where it is protected, and where it will not come into contact with anybody's shins.

There should be an unbroken gangway down one side of the room, and there should be no steps at all. If a rise or descent is necessary this should be effected by a slope. Steps are always difficult to negotiate in a darkroom.

Another device that will be appreciated by the workmen is a low three-wheel truck, on which crocks can be placed for removal from the mixing to the chilling room, and from this to the wash, etc.

A weighing room is a great advantage. In this can be kept stocks of gelatine and chemicals for immediate use, and, of course, the balance. It will be found more convenient if this room is entirely separated from the mixing room; but a great convenience is a light-lock hatch, large enough to contain one or two crocks. With such an arrangement, an operator can weigh out the necessary gelatine and chemicals into the crocks, place them in the hatch, close his door and signal to the workman, who can remove them and place them in the tanks. This considerably facilitates work and saves carrying the crocks.

The light in the weighing room may be a bright orange, not white, light, as this accustoms the eyes more readily to the darker light of the mixing room.

As is doubtless customary in most factories, a record sheet should always be kept in the weighing room, on which the operator should enter the record of the emulsions made. The following are actual examples of two which have been used:

BATCH	DATE	EMULSION	MIX	CHILL	REFRIG.	TEST	REMARKS
1340	2/2/20	Neg. A	11 A	3 P	4 P	O. K.	Store

BATCH	DATE	EM.	AG	BR	I	GEL	NH	MIX	REFRIG.	WASH	REMARKS
1880	2/2/20	Tr	500	400	5	875	100	10 A	1 P	3/2-4	Standard

Coated 2/6/20

It will be seen that the latter contains practically almost all the information required to enable anyone to make the emulsion, as it contains the actual quantities used, and the approximate time of digestion between the mixing and refrigeration. Therefore such a record obviously must not be left about for every one to read. At the same time it considerably lightens the work of the cost clerk, as reference to other records is not necessary. The first record, on the other hand, conveys but little information, except to those familiar with the actual formula of the emulsion known as "Neg. A."

In connection with the first sheet, another record was kept by the man in charge of the washing room, who also controlled the store and prepared the emulsion for coating. His sheet recorded the number of hours of washing, the temperature of the water, the weight of the melted emulsion, any additions made, and the quantity sent to the coating room. Here there was recorded the quantity of glass coated, in its various sizes. Another sheet kept by the foreman of the cutting and packing room gave the quantity of plates cut and packed, and the number of rejects. It was thus possible to check up with considerable accuracy the cost of the plates.

Possibly some explanation of the entry "Test: O. K.," in the first record, is in order. The foreman in charge of the washing room, as soon as the shreds had drained, melted a small quantity and coated two or three plates, usually 8½ x 6½ inches. The next day these were tested by the standard Hurter and Driffield method, and this gave a record as to whether the emulsion was up to standard speed, gamma infinity, K and fog reading. This formed a guide as to the fate of the batch; if O. K., it was treated as usual, the necessary additions made, and sent to the coating room. As an example of the foreman's record sheet, the following is given:

BATCH	BULK	COATING ROOM	NO.
1340 1341 1342	40,000 g	2/6/20	20946

This gives the number of the batches combined to form a coating, the date and the coating number, this last being handed on to the coater who completed the tale thus:

BATCH	DATE	COATED	REJECTS	REMARKS	STOCK
20946	2/6/20	120 8×10	10/12 8×10	Thin. More spots than usual	2/9/20
		300 1/1	2 1/1		
		600 d/h			
		300 4/4	3 4/4		

The coater's record was sent with the plates to the cutting room and the last three columns were here recorded, giving the number of rejected plates in dozens and the reason. Possibly it may be as well to explain that 1/1 means whole plate (6½ x 8½); d/h, double halves, or 6½ x 9½; and 4/4 the whole plates that were cut into 1/4 plates (3¼ x 4¼).

The stock-room sheet recorded the date of the receipt of the plates from the packing room, and also when and to what order they were issued, thus:

BATCH	DATE	ORDER	SIZES	DATE	STOCK
20946	2/9/20	2701	6 gross 8 × 10	3/10/20	20 gross

This requires but little explanation except possibly the last column. This gives the number of boxes left in stock. Naturally this does not mean the counting of the boxes as each order is cleared, but each bin had its card with a column for entry of the stock added and another for that sent out, so that the stockkeeper could balance at any time. This should be done at least once a week and Saturday morning is a convenient time, as then the record of plates wanted can be sent to the emulsion maker, who can arrange the next week's work.

CHAPTER II

THE MATERIALS USED

WHETHER there is any real difference in the action of the various halides is an open question. Theoretically there should not be, if used in equivalent weights; but practice certainly proves that there is a difference, which is probably due to the different solvent action of the excess bromides on the silver halide, or to the fact that ammonium bromide, for instance, is dissociated by heat [1] into hydrobromic acid and ammonia. This is noticeable even at 30° C. (86° F.), though with half an hour's boiling only 0.4 g of hydrobromic acid is formed from 100 g of ammonium bromide; with potassium bromide such dissociation is not noticeable. For the acid or boiling process, the ammonium salt is usually preferred.

Sodium bromide is rather hygroscopic, without being deliquescent, and thus soon forms a hard compact lump that requires a chisel and hammer to break.

Of the iodides, the potassium compound is far more stable than the ammonium, which soon decomposes, giving off iodine, which colors the salt more or less yellow. The former is more generally used, though some old workers pin their faith to ammonium iodide and decolorize it by adding ammonia, their contention being that this gives better results than either the colorless salt or the potassium compound. There is but little actual truth in this statement.

Of the chlorides, there is no choice between the sodium and ammonium salts; potassium chloride is but rarely used. For development (gaslight) emulsions, special chlorides, such as strontium, etc., are used, on the ground that they give different colors, but there is little foundation for this statement.

Ammonia, which, as is well known, is a solution of the gas in water, varies considerably in strength, according to the way in which it is kept and the number of times the bottle is opened. When the ammonio-nitrate of silver is used, slight variations are of no moment, as reduction of strength merely means using a little more solution, with necessarily increased bulk. But when a formula is used in which a definite amount of ammonia is prescribed, reduction of the strength may lead to some variations in the results, though these should be but slight and of no practical importance. In England, it is usual to call for an ammonia of 0.880 specific gravity, which is supposed to contain 35 per cent of the gas NH_3, whereas in America the stronger ammonia water has a sp. gr. of 0.90 and contains 28 per cent, therefore the latter is one-fifth weaker. There is one point in connection with the ammonia which is of importance; that is, there should be entire absence of pyridin and other tar bases, such as pyrrol and anilin. These are almost certain to cause fog. They may be tested for by adding 3.5 ccm of the ammonia water to 20 ccm of nitric acid and carefully evaporating on a water bath. The residue should be quite colorless.

Ammonium nitrate is occasionally used and the only impurity that is likely to cause trouble is the nitrite. This can be tested for by dissolving one gram in 20 ccm of water, adding one ccm of sixteen per cent sulphuric acid and one ccm of freshly prepared *colorless* one per cent solution of metaphenylendiamin hydrochloride. No yellow color should develop, indicating less than 0.00055 per cent of nitrite. If the solution of metaphenylendiamin is already colored, it should be decolorized by warming with animal charcoal and filtering.

Practically it may be stated that now, if pure chemicals are demanded, they are obtained of sufficient purity for emulsion purposes, especially as many firms make a specialty of catering for photographic chemists.

The silver nitrate is the most important salt, and if this be obtained from those refiners who make this specially for photographic work, usually a perfectly satisfactory neutral salt is obtained, the so-called " triple crystallized." The impurity to be feared is silver nitrite, which not only causes fog, but also reduction in speed.

GELATINE. — Possibly it is not exaggerating matters when it is stated that of all the ingredients of the emulsion, gelatine is the most important. Various methods have been suggested from time to time to test the suitability of this material for emulsion work. For instance, H. W. Vogel recommended heating a ten per cent solution with ten per cent solution of ammonio-nitrate of silver. If the solution turned yellow to brown it was unsuitable, giving plates that were foggy and devoid of keeping properties. Another suggested test is to add silver nitrate to ten per cent gelatine solution, cast into beakers, and expose to light. The quality of the gelatine is based on the absence of opalescence and a purple color; mere yellowing can be ignored. Both these tests are of very little value, for only in the case of printing-out emulsions is free silver nitrate ever in contact with gelatine, and there is certainly no gelatine that does not contain minute quantities of chlorides and sulphates, which are sufficient to cause opalescence.

So far as the writer is aware, there is one and only one reliable test for a gelatine, and that is to make a batch of emulsion with a sample of it under the conditions followed in practice. Every gelatine maker knows, and quite possibly every emulsion maker, that " one man's meat is another man's poison." A batch of gelatine rejected by one maker, as useless, may be accepted by another and found to give excellent results. F. F. Renwick, who was for many years chemist to the Ilford Co., of London, says:[2] " Among the raw materials of the photographic industry, the three which call for the greatest care, judgment and experience in their selection and use are gelatine, paper and collodion cotton. There are no generally recognized methods of testing any of these products for photographic purposes except the obvious one of trying them on a small scale and noting the results before proceeding to large-scale use, and it must be admitted that at present there seems little prospect of devising really reliable chemical methods of testing them."

Gelatines may be roughly divided into three classes, hard, medium, and soft, and these can be differentiated by their setting and melting points and the quantity of water they will absorb.

Various methods have been suggested for determining the setting point. The crudest is possibly that of making a solution of known concentration, say ten per cent, at a given temperature, such as 50° C. (122° F.), then transferring the beaker containing the solution to a cold water bath, continuously stirring with a thermometer and noting the time when the solution sets or gels. The difficult point is to decide what one means by "setting." As the solution cools it becomes more and more viscous, and the differentiation between increase of viscosity and gel formation may vary with different observers, as much as 5° C.

A. Cobenzl[3] suggested the use of a five per cent solution in a 250 ccm cylindrical graduate, turning the cylinder on its side and noting the time taken by air bubbles of varying diameter, from 1 to 3 mm for the first increase of viscosity and 10 mm for the greater viscosity, to rise to the top, and refusal of the liquid to flow for the complete setting point. Experiments with this method proved, however, that very discordant readings are obtainable.

R. Child Bayley[4] suggested a simple apparatus for determining the melting points, which the writer has used for many years with complete success,

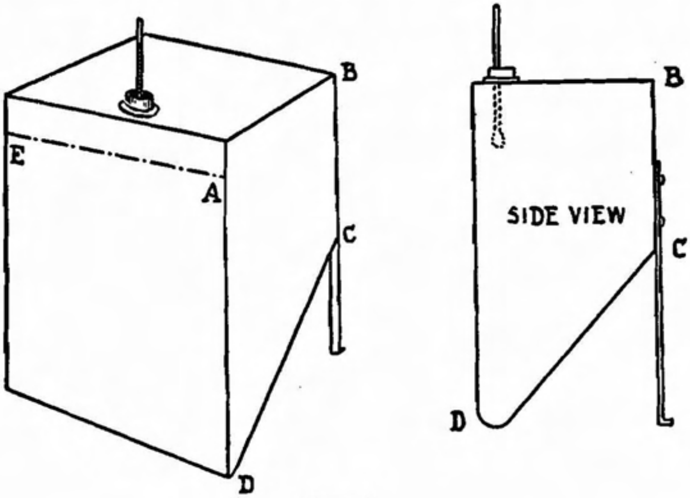

Fig. 2

the variations in the melting of a gel not being more than 0.5 per cent. This is shown in Fig. 2. It consists of a water bath of particular shape, which may be of any desired dimensions, but the sloping part *CD* must be sufficiently high to allow the placing of a bunsen burner under it to warm the water. The reason of the straight face *AD* is that no heat from the burner can travel up here, but all must pass up *CB*. The dimensions of the tank used by the writer are *AE*, 12 inches, *AD*, 18 inches, *AB*, 10 inches, and *BC*, 9 inches. Copper was used, except for the back legs, which were of iron. On the top face, in the center, was fitted a small brass ring in which fitted a cork, through which passed a thermometer, the bulb of which was just level with the ruled line, this being one and a half inches from the top of the tank. A small motor actuated a little propeller blade that worked in the center of the tank, four inches below the top, so as to keep the water in good circulation.

To use this the tank is laid on the side *BC* with the face *AE* up, and small disks of gelatine are cast on this face on the line *AE*. To make these disks a ten per cent solution of gelatine should be prepared and cooled down to about 35° C. (95° F.). Small circles of paper should be made, one half inch in diameter and about one half inch in height. The easiest way to make these is to procure a short round stick, one half inch in diameter, and some gummed labels, and cut the latter to the half inch width. They must naturally be nearly two inches long. Then wrap the slip of label round the stick, with the gummed side outside, and stick one end to the other. These little paper tubes should be placed on the line ruled on the face *AE*, and with a pipette enough of the gelatine solution should be run into them to fill them to the depth of about one quarter inch. The gelatine soon sets, when the tank should be placed on ice and left for some hours so that the disks may become thoroughly firm; about four hours is enough. The tank should then be brought out and the paper cut through with a sharp penknife, which can easily be done without injuring the disk of jelly in any way. The tank should now be set upright, filled with water, the gas burner lit, the motor started, and the thermometer placed in position. Four disks should be used for each sample of gelatine, and as the temperature of the water rises and gets near the melting point, which varies from about 24° C. (75° F.) upwards, the disks should be carefully watched. As soon as the melting point is reached, the little disks will be seen to slip down the face of the tank, and the temperature is at once read off. The mean of the four temperatures may be taken as the melting point. The only points to be careful about in this test are always to use a definite strength gel and a constant disk thickness for each test, though the actual thickness of the disk is of little moment.

W. Gamble [5] advised a more elaborate and a little more accurate method, but it is an open question whether such accuracy is required for emulsion making. The apparatus consisted of a glass beaker of one liter capacity, which was fitted with a wooden lid that served as a support for a test tube 17 x 5 cm and a stirring rod of twisted glass which acted as a screw of coarse pitch. The test tube was also fitted with a wooden lid, through which passed a thermometer graduated to tenth degrees Centigrade and a stirring rod of similar form to the outer one but of smaller diameter. To each of these stirrers was attached a small pulley wheel, both being connected by cords to the driving wheel of a small motor, supported on a vertical stand. The beaker rested on an asbestos-covered stand attached to a retort stand, and underneath was placed a bunsen burner. Capillary tubes of 3 x 10 mm, with walls of 0.3 mm thickness, were used. A definite gel strength should be used, five per cent being the best. The clean and dry capillary tubes were filled to about half their length with the gelatine solution and were then tilted on their sides so that the liquid ran into the center of the tube. The tubes were then laid on their sides under a bell jar and allowed to set for some hours, a beaker of water being placed under the bell jar to keep the air moist and prevent the formation of a skin on the jelly. It is also advisable to place the bell jar in an ice room, and to adhere to a constant time of chilling.

The beaker and the test tube were filled with cold water, heat applied, and a capillary tube attached by rubber bands to the thermometer, which was then placed in the test tube and the stirrers set going. When the temperature of the water is near the melting point of the gel, the surface of the latter in the capillary tube is carefully watched with a magnifying glass. When the melting point is reached, the concave meniscus changes to a flat surface, and at that moment the temperature is read off, this being taken as the melting point. The jelly will slip with increase of temperature, but the slipping point is not so reliable as the flattening of the meniscus. The temperature can be read to 0.3° C. This method would seem to be particularly suitable for the study of the effect of hydrolysis, etc.

Valenta adopted the same method as used by Pohl for estimating the setting point of fats. A drop or two of the gel was placed on the side of the bulb of a thermometer divided to tenth degrees and allowed to set, and then hung in an empty test tube in a water bath, that is, practically, a hot air bath. As soon as the temperature rises to the melting point, the small blob of jelly will run to the lowest point of the bulb. Then the thermometer was removed from the hot air bath and turned round and round slowly till the gelatine drop no longer travelled to the lowest part of the bulb, and the temperature read off.

Another method, which is rather more rough-and-ready and has the disadvantage that one must have as many thermometers as tests are required, is to procure a series of test tubes, the internal bore of which is such that not more than about 1 mm space is left between the walls of the tube and the bulb of the thermometer. These tubes are filled with gelatine solution and the thermometers inserted so as to be in the center of the gel, and then the whole put away to set. The tubes are then immersed in a cold water bath and heat applied. At the melting point, the test tubes will slip off the thermometers and sink to the bottom of the bath.

The melting point of a gel is as a rule

from eight to ten degrees higher than the setting point.

The absorption of water can be determined by weighing out a given quantity of gelatine, immersing in water for a definite time, and then pouring off and measuring the water. This, however, does not take into count adherent water. It is better to soak the gelatine for a given time, remove and surface-dry the gelatine with the aid of filter paper, and then weigh. For this purpose five grams of gelatine should be immersed in 100 ccm of distilled water, and then after a given time removed, dried and weighed. It is obvious that in such a test a constant temperature and time must be observed. The writer generally uses twelve hours in an ice room. A good gelatine is supposed to absorb from five to ten times its own weight of water.

Another point upon which stress was laid in the early days was the acidity or alkalinity of the gelatine. For the ammonia process this is of no moment, but for the boiling method it was contended that it should be acid. On the other hand, in most boiled emulsion formulas a small quantity of acid is purposely added. It would appear, therefore, that this point is not of much moment.

Some workers lay stress upon the firmness of the jelly formed by a gelatine. The best apparatus for testing this is Lipowitz's, as modified by Valenta,[6] shown in Fig. 3. It consists of an iron tray *P* provided with three levelling screws and a small plate *t* which carries the beaker containing the jelly to be tested, this plate being adjustable on the rod *R*. The device used to break the surface of the gel is a small metal disk *d*, a section of a sphere, thus ◡, which has a diameter of 16 mm and

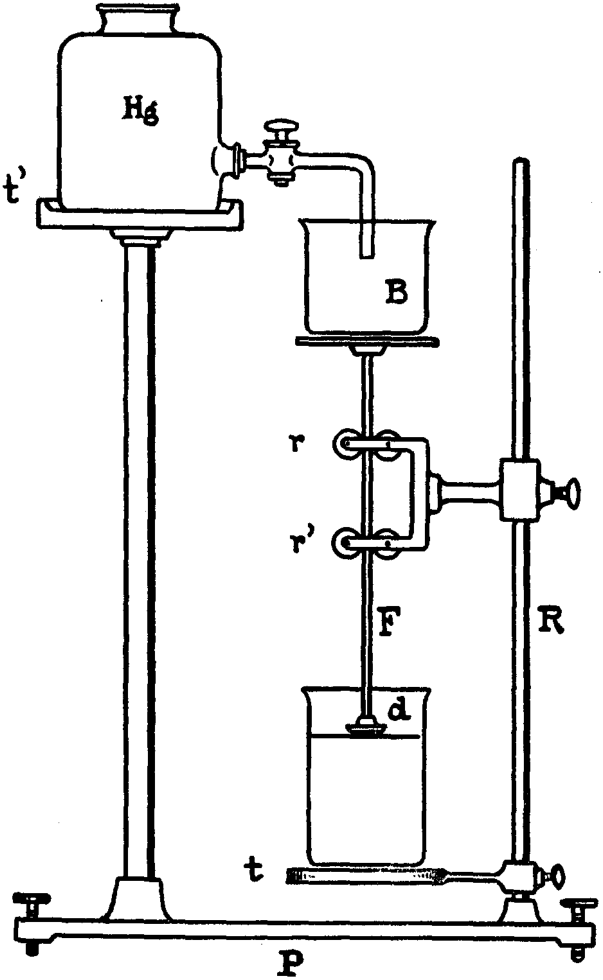

Fig. 3

a depth of 5 mm. This is fastened to a square rod ***F***, and to the other end of this rod is fastened a small metal plate, sufficiently large to carry a small beaker, or accurately graduated cylinder. This rod works between roller bearings, two at right angles to each other at *r* and the other two also at right angles to each other, but opposite to the first two at *r′*. These bearings are fastened to a metal plate which can be vertically and horizontally shifted on the upright rod ***R***, by means of a screw, as with the arms of an ordinary retort stand. At the other end of the base plate is an upright rod with table *t′*, on which can be placed a bottle containing mercury. This bottle is provided with a tubulure with stopcock, the end of the pipe being turned over.

To use this apparatus, the base-plate is first levelled. A small beaker four or five centimeters in diameter, containing 50 ccm of the jelly, is placed on the lower table and the pressure disk *d* is brought into the center of the jelly, so as just to touch the surface. The stopcock of the mercury bottle is then opened and the mercury allowed to flow gently into the upper beaker ***B*** until the surface of the jelly breaks. The weight of the rod, upper table and beaker being constant, one has merely to weigh the mercury to obtain the breaking strain. If, instead of the beaker, one uses a graduated cylinder, it is only necessary to read off the cubic centimeters of mercury used and multiply by the specific gravity of mercury, 13.56, to obtain the weight.

Valenta advises that the beaker of jelly should be allowed to stand at room temperature for from twelve to twenty-four hours and then brought to 15° C. (59° F.) by placing in a water bath. A good hard gelatine for emulsion work should have a breaking strain of 1500 grams.

PURIFYING GELATINE. — Various processes have been suggested for purifying gelatine prior to its use for emulsion making, many of which are quite unsuitable for commercial work, as for instance its purification with albumen. For this purpose white of egg equal in weight to half the weight of the dry gelatine was to be added to a solution below 49° C. (120° F.), and the whole beaten to froth and boiled till the albumen coagulated, and then filtered. Or the froth formation might be omitted and the mixture merely boiled. Obviously this is only feasible for an experimental batch. Not much more useful is Blanc's method of dissolving the gelatine and precipitating with alum and citric acid, as in this case one has obviously to get rid of the acid and alum. Henderson recommended washing the gelatine with a one per cent solution of bromide, and claimed that this gave very much better and cleaner plates; but the obvious explanation is that the whole of the bromide was not washed out.

Washing the gelatine is certainly an advantage in many cases and, provided allowance be made for the water absorbed, there is no reason why it should not be adopted in large scale work, particularly for lantern slide emulsions. Von Hübl has proved the presence of sulphurous acid or sulphites in gelatine by their action on dyes in filter making, and should these exist in gelatine, washing would obviously remove them. J. B. B. Wellington[7] stated that sodium sulphite in the presence of ammonia reduced the silver bromide and caused the formation of a mirror. But he used four parts of anhydrous sulphite to ten of silver nitrate and dissolved the precipitate with ammonia, thus probably using an ammoniacal solution of silver sulphite. On the other hand, sodium sulphite in minute quantities was used by Valenta for obtaining fast fine-grained emulsions for the Lippmann process (see p. 131), and the writer has used it for making slow emulsions without ill effects. The ratio in the latter case was 0.25 to 100 silver nitrate, converted into ammonio-nitrate, and this emulsion was digested for one hour at 43° C. (110° F.) and two hours at 27° C. (80° F.) before being set on ice. In all cases the results were regular, very clean, and gave a speed of 22 H. & D. with high gamma infinity, the fog reading with ten minutes development with the standard pyro-soda developer being only 0.1.

One of the legends that has persisted from quite early days is that some gelatines contain grease, which is the cause of matt-looking spots and pits on the plates. Washing with benzol, precipitation of a solution with alcohol, allowing to set to a jelly and cutting off the top, saponification with soap, oxgall or ammonia are some of the remedies proposed. But there is no proof that fatty matters exist in gelatine, and a direct experiment was carried out by A. J. Brown,[8] who purposely added oil to an emulsion and obtained no pits.

It has already been pointed out that the practical test of a gelatine is the most reliable, but there are certain factors which should be taken into account. In the first place, the ash content should not be too high. A safe limit is two per cent, at which any alkalis, sulphites, chlorine or phosphorus compounds are harmless. Most to be feared are traces of metallic salts, particularly those of iron, copper, lead and zinc, and these should not exceed fifty parts per million. Aluminum, if found in greater quantity than 0.106 per cent, shows that the gelatine has been hardened by treatment with alum and may give trouble.[9]

Sulphur compounds, calculated as SO_2, should not exceed 0.1 per cent, and may be determined by distillation, collecting the distillate in solution of iodine.

The recent paper by S. E. Sheppard, of the Kodak Research Laboratory,[10] is the most important contribution to the science and practice of emulsion making yet published. The following is but a brief resumé. R. F. Punnett, of the Eastman emulsion department, proved that from an active gelatine, that is, one which gave high-speed emulsions, an extract could be prepared which, when added to a relatively inert gelatine, gave rapid emulsions. An investigation, extending over many years, that included exhaustive tests of the raw materials at every intermediate stage, finally ran to earth the mysterious "Gelatine X," which proved to be the cause of high sensitivity. This was allyl isothiocyanate, $C_3H_5.NCS$, or allyl mustard oil.

The isocyanates or thiocarbamides react with ammonia and amines, forming thiocarbamides, $CS.NHR.NH_2$, in which R is an allyl or ethyl molecule. Sheppard considers that although allyl thiocarbamide is the active sensitizing material, it is not in itself, nor in its combination with the silver salt, the actual substance of the sensitivity centers. The silver compound may be considered as $(AgBr)_m.(CS.NHR.NH_2)_n$, in which m and n are simple integers, probably 2 and 1 respectively. In the presence of alkalis, this compound splits up into silver sulphide, cyanamide, guanidine and alkaline bromide, to the first named being ascribed the actual sensitiveness. But this must form nuclei discretely and not above a certain size.

Other compounds, such as sodium thiosulphate (hypo), sodium selenosulphate (Na_2SeSO_3), potassium tellurotellurate ($K_2Te_2O_3$), are effective sensitizers, as is also potassium isoselenocyanate. All these combine with the silver halides to form decomposable complexes.

The quantity of these sensitizing substances required is extremely small, 1: 1,000,000 to 1: 300,000. The action reaches a maximum effect for a certain quantity and then decreases as the amount of the active material is increased, with corresponding increase in fog.

Applications for patents for the use of these compounds have been made.

On the publication of this paper, reports by other firms were at once published as to researches that they had carried out. MM. Lumière[11] stated that they had examined about nine hundred substances as sensitizers and found that aesculin, codein, thebain, diethylenediamin, thiocarbamide and guanidine sulphocyanate could be advantageously used. This fact had not been published, as the method had been used commercially.

In connection with this it is interesting to note that H. J. Newton[12] recommended an infusion of tea and mustard seeds, one of the raw products used by Sheppard, as a preservative for dry collodion plates, and stated that increased sensitiveness was thus obtained compared with those plates for which tea alone was used. Laudanum and the alkaloids obtained therefrom were also used with the same plates, and codein and narcotin, two of the opium alkaloids, have been well known as sensitizers for washed collodion emulsion. These do not contain any sulphur molecules. Undoubtedly there are other compounds which will act in the same way, though they have not yet been detected.

A valuable paper on the use of various bromides in emulsion making was published by B. H. Carroll & D. Hubbard[13] and full tables as to the grain size, fog and gammas obtained. This is apparently only the first of a series which is to be published under the authority of the Bureau of Standards.

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[1] Eder, *Ber. Akad. Wiss. Wien.*, 1880; *Phot. Woch.*, 1881, 74; *Handbuch*, **3**, 19.

[2] *Annual reports J. S. C. I.*, 1921, **6**, 542.

[3] *Jahrbuch*, 1914, **28**, 70.

[4] *Phot. J.*, 1896, **36**, 224.

[5] *Brit. J. Phot.*, 1910, **57**, 668.

[6] *Jahrbuch*, 1909, **23**, 179.

[7] *Phot. News*, 1885, **29**, 223.

[8] *Phot. News*, 1882, **26**, 103.

[9] For methods of testing gelatine see R. M. Mehurin, *Ind. Eng. Chem.* 1923, **15**, 942; "Glue and Gelatin," J. Alexander, 1923, Chap. X. For general information see the two volumes entitled "Gelatine" by S. E. Sheppard, in the series Monographs on the Theory of Photography, published by the Research Laboratory of the Eastman Kodak Company, also "The Silver Bromide Grain of Photographic Emulsions" by A. P. H. Trivelli & S. E. Sheppard, in the same series; "Leim und Gelatine," R. Kissling, Stuttgart, 1923; D. Kruger, *Phot. Ind.*, 1928, **26**, 196, 227, 264.

[10] *Phot. J.*, 1925, **65**, 380; *Brit. J. Phot.*, 1925, **72**, 481; abstracted in *Amer. Phot.*, 1926, **20**, 219.

[11] *Rev. Franc. Phot.*, 1925, **6**, 291; *Brit. J. Phot.*, 1925, **72**, 634; abst. in *Amer. Phot.*, 1926, **20**, 219.

[12] *Anthony's Phot. Bull.*, 1874; *Bull. Soc. Franc. Phot.*, 1874, **16**, 39.

[13] *J. Phys. Chem.*, 1927, **31**, 906.

CHAPTER III

MIXING THE EMULSIONS

THERE are two main methods of mixing emulsions, the acid or boiling process and the ammonia method. Which is the better is an undecided point, some pinning their faith to one and some to the other. Some advocates of the acid process contend that plates coated with emulsion made by this process keep better than those made by the other. On the other hand, it is stated by the adherents of the ammonia method that this gives the highest sensitiveness.

Before proceeding further, it may be as well to impress upon the amateur emulsionist that there is absolutely no assurance, because good results are obtained from any particular formula when used in a small batch, that equally satisfactory results will be obtained commercially when large batches are made. Nor does it follow as a matter of necessity that any stated result will be obtained from any given formula, and this applies to small and large batches. The factors that can vary are so many, and the results may be so different, that one is almost tempted to believe that some serious error in formula or manipulation has been committed. The factors in mass production are so altered that small batches may be looked upon as mere sign posts showing the direction in which one may work, but not telling one how far one is from the distant goal. Even the transference of a formula from one factory to another may mean considerable experimenting to fit the new and in most cases unknown factors to the given process, or the reverse.

To the beginner in emulsion making, the soundest advice that can be given is to avoid striving for high-speed emulsions, at first at any rate. It is infinitely easier to make a good slow emulsion than a good fast one, and while transparency emulsions will probably not content the tyro, it is just as well to start with these to learn the principles and manipulations, and then try for faster results, and even then to be satisfied with what would probably be called slow negative emulsions, that is up to about 150 to 200 H. & D.

There are several factors that have to be taken into account which it is as well to clear up before starting on further details.

THE QUANTITY OF GELATINE. — The first point to be recognized is that gelatine acts as a protective colloid and prevents not only the formation of a coarse grain, but also fog. The former action can be at once proved by taking two tall graduates, the one containing a warm solution of potassium bromide, say ten per cent, and the other containing a warm ten per cent solution of gelatine containing ten per cent of potassium bromide. On adding to each the same quantity of a five per cent solution of silver nitrate and shaking well, it will be found that totally different results will be obtained. In the aqueous solution there is immediate formation of thick white curds or flocks, while in the gelatine solution a perfectly smooth liquid is obtained, something like cream. A drop of the latter placed on a sheet of glass and examined by transmitted light will be seen to have almost a blood-red color without the slightest suspicion of grain. If the two graduates are kept warm and left for a short time, it will be seen that the aqueous solution will deposit the silver bromide in a very few minutes, while the gelatine solution will remain milky for hours.

For slow emulsions, particularly for transparency work, it is advisable, therefore, to use a fairly high proportion of gelatine, during the mixing, as this helps to keep the grain fine, and high speed is not required. With slow negative emulsions also, a fairly generous quantity of gelatine can be used. If rapid emulsions are required, the less gelatine used, within certain limits, the better.

One rule laid down in the early days of emulsion making was to use one-fifth of the weight of silver nitrate in gelatine for the mix, and in the boiling process to add every half hour one-fourth of that used in the mix, and as soon as the digestion was finished to add gelatine equal to double the weight of the silver used. The idea was that as the silver salt becomes coarser or more crystalline, more gelatine is needed to " carry " it, or, in other words, to prevent it from becoming too coarse-grained.

The addition of the gelatine after the digestion is based on the supposition that the gelatine is much decomposed during this time. There must be, of course, some decomposition by the heating, whether in acid or ammoniacal solutions, but it is open to very grave doubt whether it is so pronounced as to be an element of danger. The change in setting point of a gelatine boiled with a small quantity of acid for an hour or two is at the most only about 2° C. With ammonia digestion at 50° C. for five hours, the setting point was only reduced 3° C. It would probably be more correct to state that the gelatine is hydrolysed, possibly into Hofmeister's semi-glutin and hemi-collin, to a small extent, and the former does reduce silver nitrate; but one has to take into consideration that we are dealing with the halides in presence of excess of alkaline halide, which would certainly tend to protect the silver bromide from reduction.

The smallest quantity of gelatine used in the mix was probably by W. K. Burton, who reduced it to one eight-hundredth of the total bulk of the mixing liquids. In some of the precipitation methods, also, small quantities of gelatine were used, though in these processes the silver bromide was precipitated and rapidly washed and then re-emulsified in the full quantity of gelatine.

THE RATIO OF BROMIDE. — Theoretically it should be possible to make an emulsion with the exact equivalent weights of silver nitrate and bromide. But should any error occur in the weighing of the salts so that the silver was in excess, the emulsion would be spoilt through fog. The exact excess of bromide varies with different experimenters, and assuming in each case that ammonium bromide is used, the following table shows the ratios advised and the excess:

	SILVER	BROMIDE	EXCESS
Abney	100	73	15.4
Bennett	100	63.6	6.03
Burton	100	59.5	1.9
Debenham	100	115.2	57.6
Eder	100	66	8.4
Eder	100	125	67.4
Eder	100	133	75.4
Eder	100	150	92.4
Newberry	100	72.17	14.57

Too much stress must not be laid upon these figures, and it will be found that the excess of bromide varies with almost every worker and every emulsion formula. That a fairly large excess of bromide is favorable for the attainment of a high speed is now generally acknowledged.

The explanation usually accepted for the favorable action of the excess bromide is that the finer particles of silver bromide are dissolved by the excess and in the course of ripening are deposited on the larger grains, thus giving increased sensitiveness.

THE ADDITION OF IODIDE. — The use of iodide, in negative emulsions at least, is universal. Those containing iodide are more opaque, and less likely to suffer from halation and solarization. The ratio of iodide to bromide differs considerably, and may vary from one to five per cent of the total silver halides.

Eder[1] says: "If iodide and bromide of potassium (or ammonium) are dissolved in gelatine and water, and silver nitrate be added to this mixture, the formation of bromo-iodide of silver takes place at once; a kind of double compound appears to be formed, at least the behavior of such silver bromo-iodide differs from that of silver iodide and silver bromide separately prepared and then mixed. A bromo-iodide emulsion that has been digested for a sufficiently long time is more sensitive than a pure bromide emulsion and more to gaslight than to daylight. At present many good commercial emulsions are prepared with bromo-iodide, in which the manufacturers use silver iodide to the amount of from one to five per cent of the total silver bromide, and Eder also recommended this addition for boiled emulsions in the earlier editions of this work.

"Yet some leading makers prefer pure bromide emulsions, because beautifully detailed portrait plates can be thus obtained, which develop and fix quickly. The question as to whether pure bromide or bromo-iodide emulsions are more suitable for portraits has not yet been definitely decided. In Germany, Austria and France more pure bromide emulsions are made, in England perhaps more bromo-iodide, but with a small iodide content, which, however, makes the plates a deep egg color.

Emulsions with ten per cent of iodide are not commercially met with, because they give as a rule thin negatives which are difficult to develop.

"For landscape work bromo-iodide emulsions, with three to four per cent of iodide, are decidedly better than pure bromide emulsions, because halation is less with the former and small details against the sky are better differentiated. Generally it may be stated that an emulsion with a small proportion of iodide permits of greater latitude in exposure. With greater iodide content, the sensitiveness can be greatly increased by continued digestion, but the pictures become flat in the high-lights and are wanting in brilliancy and vigor. As the iodide acts as a fog preventive, bromo-iodide emulsions can be digested longer without the fear of fog. The practically permissible content of iodide in the bromide emulsion varies from one to six per cent, that is to say to every one hundred parts of bromide from one to six parts of iodide may be used. This applies to the ammonia as well as the boiled emulsions.

"In the ammonia emulsions for ordinary portrait work, no iodide, or at the most one to two per cent, is advisable, in order to keep the plates clean. Above five per cent no advantage can be observed, as the brilliancy and plasticity of the plates suffer. The author (Eder) found ten per cent of silver iodide too high, because the images become very thin and cannot be developed with ferrous oxalate, and density is only obtained with difficulty with pyro. Since emulsions so rich can be digested even at 50° to 55° C., great sensitiveness can be obtained, and Scolik[2] and Burton[3] prepared rapid emulsions by this method.

"In the acid boiling process a small portion of iodide is favorable, although many adhere to the pure bromide emulsions. The author (Eder) recommends from three to five per cent of silver iodide. Silver iodide in small quantities, one twenty-fifth to one fiftieth, produces an increase of the sparkle of the high-lights and a more delicate gradation of the negative, it favors freedom from fog, delays development and gives with sufficiently long development more details in the shadows; in greater quantities, about one twelfth, a considerable loss of vigor makes its appearance, which is more noticeable with the oxalate developer than with pyrogallol. The pyro developer is more suitable for emulsions rich in iodide than ferrous oxalate. In the cold emulsification process, according to Henderson, a greater content than one to two per cent is prejudicial. Although bromo-iodide of silver shows a considerably greater sensitiveness than pure silver bromide, yet the sensitiveness in photographing pigments in the camera is the same for the two, as also for the yellow light in the dark room."

It should be noted that the above passage was written in 1903, and therefore some of the statements, particularly as to the fashions in emulsions, are hardly correct at the present time.

The statement as to the formation of a complex of bromide-iodide of silver would also seem, in the face of the experiments of F. F. Renwick & V. B. Sease,[4] to be erroneous. By a process of sedimentation of emulsions it was found that the percentage of silver iodide and of coarse grains in the lower strata of emulsions, allowed to settle, was much higher than in the upper strata. Reference to the original should be made for details.

How to Add the Iodide. — A great deal depends on the method of mixing of the emulsion and the way the iodide is added. In the first place it must be accepted as an established axiom that if the three halides, iodide, bromide and chloride, are mixed together and silver nitrate added, there is always a precipitation in the order iodide, bromide and chloride, though this does not preclude the formation of a complex of silver iodide-bromide in a mixture of these halides. As bearing on this point it may also be noted that a silver chloride plate immersed in an alkaline bromide solution is converted into bromide, the bromine wholly or partially replacing the chlorine. In the same way a pure bromide plate, treated with iodide, is converted into silver iodide. This can be proved in that the plate, after treatment with the iodide, can not be developed with an ordinary developer. The plate converted into bromide will not develop with sodium quinone sulphonate plus sulphite, whereas silver chloride is readily reduced by this mixture.

Eder has also proved that a separately prepared silver iodide emulsion, mixed with a separately prepared bromide emulsion, gives a spectral sensitiveness curve different from that of an emulsion which contains both iodide and bromide at the moment of mixing. The former shows a drop in the sensitiveness curve on the more refrangible side of the G line, while with the bromo-iodide emulsion the curve is continuous.

If the two halides are present in a gelatine solution in the normal ratios, it is obvious that the iodide must be as widely diffused throughout the solution as the bromide, and if the latter is in excess, say in the ratio of twenty to one, it seems absurd to suppose that the silver nitrate would not combine in these ratios with the halide that it comes into contact with. One cannot imagine free silver nitrate sailing around and waiting till it met with the iodide before combining with the bromide that it would inevitably meet. It seems reasonable, therefore, to assume that a complex of bromo-iodide is formed rather than pure bromide and pure iodide. Trivelli and Sheppard,[5] in dealing with the crystallization of silver bromide, state: "The above mentioned emulsions (and this may be said of practically all highly sensitive emulsions) contain in addition to the silver bromide a certain quantity of silver iodide, which varies in different emulsions. But there is never any indication that either bromide or the iodide crystals are precipitated alone — i.e., without an admixture of the other. In investigating this question, 122 photomicrographs of as many emulsions, prepared in various ways and magnified 2500 times, were examined without finding one instance of separate precipitations of the iodide and of the bromide, — i.e., of hexagonal silver iodide and regular silver bromide."

The general practice would seem to be to add the soluble iodide to the bromized gelatine, but in some cases it is added to the mixed bromide emulsion. The reason for this procedure is that silver iodide is very apt to form a coarse granular precipitate, and, by adding the iodide after the formation of the bromide, with which a finer grain can be more easily obtained, there is less chance of coarseness, as the soluble iodide converts the silver bromide into iodide. But Eder states that potassium iodide added to the ready-formed bromide in the presence of excess bromide converts the bromide only very slowly, and that after half an hour's digestion by boiling, considerable quantities of potassium iodide exist, and these delay the process of ripening. The presence of the iodide can be proved by precipitating the emulsion with alcohol, when the potassium iodide can be qualitatively proved in the latter. This statement is a little difficult to understand in the face of the fact that treating a plate with iodide, even a one per cent solution, for five minutes is sufficient to convert practically the whole of the bromide to iodide. That the presence of excess of bromide might delay the conversion is conceivable.

The addition of iodide to an already-formed bromide emulsion certainly delays ripening, but the author has found that, provided digestion be prolonged, an equally fast emulsion can be obtained as when the iodide and bromide are in the mix, and there is less fog. On the other hand the addition of iodide to an emulsion just before setting appears to slow the emulsion considerably.

One argument advanced in favor of the addition of iodide after the mix is that in this way every grain of silver bromide is attacked and the result must be the existence of nothing but grains of bromo-iodide; but the same argument might well be applied to those cases in which it was in the primary mix, as has been pointed out above.

It has also been suggested to add the iodide to the silver nitrate solution, in which it is soluble, and then to add this to the bromized gelatine. Again, some of the silver nitrate may be added to the bromized gelatine, then the iodide, and then the remainder of the silver. Practically but little difference can be detected in these modifications.

In some cases gelatine is mixed with the silver nitrate and the bromide added. This was recommended by Abney, and his formula and method of mixing was as follows:

A.	Potassium iodide	5	g
	Water	30	ccm
B.	Ammonium bromide	70	g
	Water	240	ccm
C.	Soft gelatine	15	g
	Water	360	ccm

D.	Silver nitrate	100 g
	Water	360 ccm
E.	Hard gelatine	40 g
F.	Hard gelatine	40 g

The gelatine *C* is dissolved and added to *D* at 65° C. (149° F.) and thoroughly stirred. When *B* is dissolved, if the gelatine be alkaline, a very little hydrochloric acid is added to the silver-gelatine mixture, little by little, with constant stirring, and finally *A* is dropped in. The emulsion should then be digested for half an hour at boiling temperature. During the digestion the hard gelatines *E* and *F* should be rapidly rinsed with water to remove dust and then allowed to soak in 960 ccm of cold water and melted at 38° C. (100° F.). They are then cooled to 21° to 27° C. (70° to 80° F.) and the emulsion should be also brought to this temperature, and then the gelatine added. Abney stated that he had never met with "red fog or other disease induced by this method of mixing, and we recommend it in preference to the methods indicated above."

Red or dichroic fog, which is red by transmitted and green by reflected light, was a very common "disease" in the early days of plate making, and seems to have been the chief failing. At the present day it is rarely if ever met with, which is possibly due in part to improved methods of manufacture, possibly also to the abandonment of ammonia as the alkali in development, and doubtless also to improved methods of making the gelatine. The writer has only met with it in the normal way when the emulsion has been coated very thickly on glass. It would appear to be colloidal silver or a colloidal complex, and is sensitive to light. It can also be very readily formed by immersing a plate or film in hypo solution for a minute or so and then immediately covering the plate with a sheet of glass. In this case it is obviously due to insufficient fixation, and while one is not likely to do this intentionally, it may occur by the accidental overlapping of films or plates in the fixing bath. It is not advanced that the two forms of red fog thus produced, that is the one in the emulsion and the other in the fixing bath, are the same; but they have the same appearance and behave identically with solvents such as cyanide, etc.

That a large proportion of iodide tends to give thin negatives with a given time of development is indisputable: that is to say, iodide decreases the development velocity; but the same gamma can be obtained by prolonging the development, and the author has always found that increase of iodide prolongs the period of underexposure, which in printing is the most valuable part of the negative scale.

It has also been noticed with emulsions rich in iodide that there is much slower fixation, and frequently what has been called "iodide fog," which is a slight milky appearance of the film in the fixing bath, which prolonged stay in the bath does not seem to remove. On the other hand this iodide fog disappears during subsequent washing, therefore it may be due to the formation of a double silver iodide-hypo complex, which is less soluble in hypo, or requires more water for complete solution.

It has been recorded above that Eder has stated that a bromo-iodide emulsion was more sensitive to the less refrangible rays, green and yellow, than a pure bromide emulsion. F. F. Renwick [6] showed that treatment of a plate with potassium iodide gave distinct orange and red sensitiveness, and stated that "the conferred red sensitiveness must be due to a change within the silver bromide or bromide and iodide grains rather than to anything akin to ordinary sensitizing by dyestuffs." The author [7] called attention to Carey Lea's paper on the sensitiveness of iodide and bromide of silver to the less refrangible rays,[8] in which he clearly proves that silver iodide is much more sensitive to red and orange than the bromide. R. B. Archey [9] records, with spectrograms, the red sensitiveness caused in an emulsion through an accidental overdose of iodide. S. E. Sheppard [10] proved that this peculiar action was specific and only appeared with emulsions that in themselves showed sensitiveness to the less refrangible rays, and that, therefore, the action was merely an intensification of an already existing action.

As a matter of fact this peculiar action of iodide has been known to the author for about twelve years, but it was always considered as a trade secret and never disclosed. This trade or professional etiquette, which prevents the manufacturer from giving information as to his emulsions, is a serious stumbling block in the advance of our knowledge of the real whys and wherefores of emulsion making. In the early days, and it must not be overlooked that the gelatino-bromide emulsion was discovered by an amateur, the technical journals were filled with accounts of experiments in emulsion making; but since the commercial manufacture of plates an impenetrable wall of silence has shut down, that one might as well try to pierce as get through a modern safe with a knitting needle. This is, of course, explicable and understandable to some extent in view of commercial rivalry, but there can be no doubt that much valuable information might be given without violating professional secrecy.

There is one fact that has not yet been recorded, and that is, from the writer's experiments, it appears that this red-sensitiveness is limited apparently to a particular method of emulsion making (see p. 65), and increase of the iodide ratio frequently seems to prevent its appearance. No explanation can be advanced of this, but that it is a fact has been repeatedly proved.

Schleussner and Beck[11] reported on some experiments as to the effect of the ratio of iodide to bromide, and differentiated between emulsions in which the iodide was added to a finished bromide emulsion, or the plates were bathed in iodide solution, and the results obtained by the addition of iodide to the bromized gelatine. The latter were called primary emulsions and the former secondary; the term tertiary being applied to mixtures of bromide and iodide emulsions separately mixed. When the iodide is added to a ready mixed bromide emulsion, only the outer surface of the silver bromide complex was affected, while in the primary emulsions, a double complex of bromo-iodide is assumed. Their results prove that for the primary emulsions 3.5 per cent of iodide gave the steepest gradation. With the ammonia process, in which the silver was converted into ammonio-nitrate, three to five per cent gave the best results; whereas when the ammonia was added to the bromized gelatine, one per cent was the best. For orthochromatizing with erythrosin, one per cent gave the best results, and for X-ray work a pure bromide gave faster plates than one containing iodide. These results do not jibe satisfactorily with practice, and, considering their method of testing, too much weight must not be laid on their conclusions.

MIXING THE EMULSION. — When one comes to the mechanical mixing of the emulsion a great diversity will again be found. For instance, one method is to add the silver solution to the gelatine solution containing the whole of the halides; another is to add the silver and halides simultaneously to the gelatine solution; yet another is to add the silver solution in successive portions at various stages of digestion.

It will be seen that by the first method the later portions of the bromide must be formed in the presence of less and less excess of bromide. If, as one may assume, the greater the excess of halide the slower the silver bromide, there must be in this case primarily a very slow form of silver halide followed by successive portions of more rapid, and further, if the silver be added very slowly, the first-formed halide must be subjected to a longer ripening than that formed later. This applies to the acid process. In the ammonia method, that is to say, that in which the silver nitrate is converted into ammonio-nitrate, the later-formed silver halide must be formed with increasing quantities of free ammonia, and therefore one can assume that the action of this would be super-added to the decreasing quantity of the halide. There is a variant of this process in which the ammonia content may be kept constant, and that is by adding a definite quantity of ammonia to the bromized gelatine.

In the second process, the silver halide is always formed in the presence of increasing quantities of excess halide, and it will be found an extremely useful method, as it certainly has a tendency to give fast emulsions and yet without want of density in the high-lights, or to talk in the language of the H. & D. system, there is very little tendency to the formation of the period of over-exposure.

Before dealing with the actual methods of mixing, it may be as well to lay stress upon one point, which the author considers of fundamental importance, and that is the necessity of continual stirring of the emulsion during the whole time of mixing and digestion. This is the more important the less the gelatine content. During the mixing, it is important in order to bring the silver solution rapidly into contact with the halide; and during digestion it is imperative, otherwise the silver halide will settle down to the bottom of the vessel and form a more or less coarse-grained hard cake that is extremely difficult to re-emulsify.

For commercial work, the provision of a mechanical stirring arrangement with direct motor drive, or with a grooved wheel and round belt and countershaft, is comparatively easy and by no means costly. As regards the actual stirrer, one device that has been found efficient is to use a solid silver rod with a cross piece at the end. The dimensions will naturally vary with the size of the mixing vessel, but assuming that the crock system is adopted, the cross pieces or paddles should be sufficiently long to reach within about an inch each way of the sides of the crock, and the rod be long enough to come within an inch of the bottom. The paddle need not be more than two inches broad, and the blades should be given a slight twist, propeller blade fashion. The length of the rod will depend upon the crock depth, and it should preferably be rectangular rather than round, and should fit into the end of a revolving rod, which can be brass; iron should not be used for fear of rust. The stirring rod can be fitted with a screw to fit a socket in the revolving rod, but if a screw be used the blade must revolve in an opposite direction to the thread of the rod, otherwise it will be found that the stirrer will gradually unscrew itself. It is preferable to cut a rectangular slot in the end of the brass rod so that the end of the stirring rod can be slipped into it. A couple of brass pins running through holes will hold the rod firmly, particularly if the pins are put in from opposite sides. There is just one little point about these pins that will be found useful and that is that they should have one end bent into a ring and be fastened by this with a short length of chain to the brass rod, as it is annoying to accidentally drop a pin into a crock full of emulsion and have to paddle about therein with the hands to find it. As regards the speed of revolution, this should not be too slow, about sixty revolutions per minute is satisfactory.

It is always as well in mixing emulsions, whether the acid or ammonia process be used, to run a little silver in first so as to form a small quantity of halide, and stir well for about a minute before running in the bulk of the silver, as this gives nuclei for the formation of further crystals.

Naturally every commercial manufacturer has his own particular arrangements for mixing, and these may vary from the hand pitcher to specially made glass vessels. A plan that has been found to work well in practice for all methods is shown in Fig. 4. The two upper jars are ordinary glass percolators fitted with pure rubber stoppers which should not project above the necks inside and through these should be run short pieces of glass tubing, which should also not project above the top of the stoppers, so that the liquids may be completely drained out.

These glass tubes should be provided with glass stopcocks by which the flow of the solution can be regulated, or in place of the stopcock a short piece of pure black rubber tubing may be fitted and on this one of the usual screwdown pinchcocks, such as are used in laboratory work, fastened.

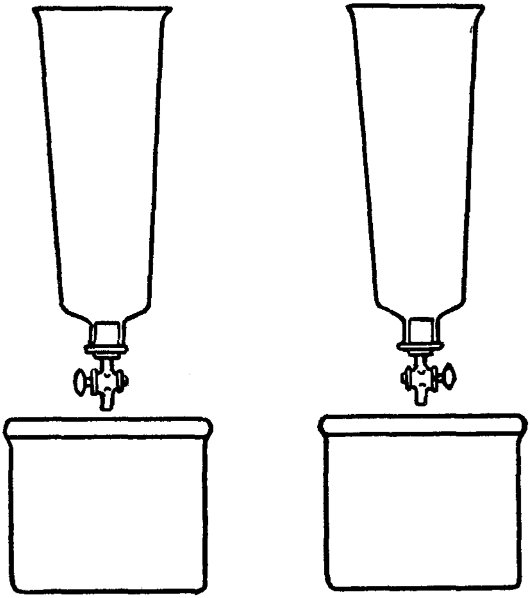

Fig. 4

If it is not convenient to have these vessels immediately over the mixing crock, they can be provided with a glass tube with two right-angled elbows, the length of the horizontal piece being such as to lead from the stopper to over the crock;

then the vessels can be supported on shelves with a hole for the protrusion of the exit pipe, or a slot may be cut in the shelf through which the neck of the glass jar can be slipped. If the bromide and the silver solutions are to be run into the gelatine simultaneously, it will only be necessary to adjust the flows by the pinchcocks. If the silver and bromide solutions are to be added at higher than room temperature, there is no difficulty in bringing them up to this temperature before putting in the percolators or the latter can even be surrounded with a hot water jacket. Naturally much will depend on the bulk of the solutions to be mixed, and when this is not too great there is nothing better than one of the commercial glass separatory funnels, which can always be obtained with a stopcock.

As regards the mixing vessel, this may be a stoneware crock, and care should be taken to obtain these with as smooth a surface inside as possible. The question as to whether lids should be obtained or not is to a great extent a matter of taste. Personally the author is in favor of lids, but they should not have a projecting edge. The most satisfactory crock met with was one made by the well-known firm of Doulton, of Lambeth, London, of yellow stoneware, which has perfectly straight smooth sides inside, is provided with two handles and has a lid that fits flush outside. These are easy to clean and handle. While the emulsion maker will naturally be careful as to the light in the work room, the writer has a fancy for providing crocks with wooden lids in which is cut a slot, so as to allow of the passage of the stirring rod. It is some comfort to know that the emulsion is practically protected from all light during the digestion period. Another and possibly a minor point: all crocks should be numbered and their weight taken and a list of these weights kept in a convenient place.

As regards the rate of mixing, this varies with the formula used. In some cases it may even be prolonged to two hours, but as a normal procedure, in the acid process a run of about one thousand centimeters in ten minutes is satisfactory. With the ammonia process this may be doubled, it being remembered that in all cases a preliminary addition of a very small quantity of the silver solution should be made as already advised.

There is one point which may arise in connection with emulsion making and that is as to the total bulk which should be mixed at once. On this point practice naturally differs with each individual maker, but the writer has always adopted one particular size batch for both negative and positive work, based on the use of five hundred grams of silver nitrate. Enough emulsion might be required to call for five thousand grams in all, but the procedure was not varied, ten batches being then made. This considerably facilitates the work of pressing, washing and making to bulk, which is naturally left to workmen.

There is one disadvantage in the use of crocks, which is that the thickness of the walls makes the operation of heating up and cooling down the emulsion somewhat slower than is sometimes desirable, but one soon learns to allow for this. The ideal mixing vessel is a solid silver water-jacketed kettle, so arranged that steam or ice-cold water may be let into the jacket, while the bottom of the kettle is fitted with an outlet valve. The whole is arranged at such a height from the floor that the crocks can be run under the outlet, and the emulsion run out at any desired stage of the process. Enamel-lined iron kettles can also be used, but they are not much better than crocks as regards rapidity of heating and cooling. They are advantageous when very large batches of slow paper emulsions are to be made. In this case, as will be seen later (see Chap. VI), these kettles can be used.

Summing up the fundamental principles of mixing emulsions, it may be stated that slow and medium speed ones should be mixed in the presence of large quantities of gelatine and water, while fast ones should be compounded with low ratios of gelatine and considerably less water. Practically one per cent is a safe limit for fast emulsions during the actual mix, with more added soon after, otherwise coarse grain and fog will ensue.

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[1] *Handbuch*, 1903, **3**, 118.

[2] Scolik (*Phot. Korr.*, 1882, **13**, 375) mixed A. potassium bromide 40 g, ammonium bromide 40 g, potassium iodide 8.3 g, gelatine 166 g, water 833 ccm; B. silver nitrate 100 g, water 833 ccm; and added enough ammonia to form a clear solution. A was heated to 40° C. (104 F.) till the gelatine was dissolved, and B added in small quantities and digested for 45 minutes in a water bath at 50° to 55° C. (122° to 131° F.) with frequent shaking.

[3] Burton (*Phot. News*, 1886, **29**, 177), gave the following formula for a

very sensitive emulsion: A. silver nitrate 100 g, water 500 ccm, ammonia to form a clear solution; B. potassium bromide 80 g, potassium iodide 50 g, soft gelatine 20 g, water 1000 ccm; C. dry gelatine 250 g, B was heated to 70° C. (158° F.) and A, cold, added with constant shaking, digested for 20 minutes at 50° C., and allowed to slowly cool. C was added after being allowed to swell for 20 minutes in water, drained and melted; the emulsion was then set and washed. Still higher sensitiveness was obtained by digesting at 70° C. (158° F.) with frequent agitation and, after addition of the gelatine, precipitating with alcohol.

[4] *Phot. J.*, 1924, **64**, 360; *Brit. J. Photo.*, 1924, **71**, 587; abst. *Sci. Ind. Phot.*, 1924, **4**, 157; *Amer. Phot.*, 1925, **19**, 56. The results obtained are probably only due to a particular method of mixing the emulsion.

[5] "The Silver Bromide Grain of Photographic Emulsions," 1921, 79.

[6] *Phot. J.*, 1921, **61**, 13.

[7] *Brit. J. Phot.*, 1921, **68**, 129.

[8] *Brit. J. Phot.*, 1875, **22**, 256; *Bull. Soc. Franc. Phot.*, 1875, **21**, 236.

[9] *Phot. J.*, 1921, **61**, 235.

[10] *Phot. J.*, 1922, **62**, 88.

[11] *Zeits. Wiss. Phot.*, 1921, **22**, 105.

CHAPTER IV

NEGATIVE EMULSIONS

As already stated, there are two main methods of making emulsions, the acid or boiling process and the ammoniacal, and the main points have already been dealt with. In this chapter the actual formulas will be given, first for the acid process.

SLOW NEGATIVE.—

Ammonium bromide	350	g
Potassium iodide	9	g
Gelatine	250	g
Hydrochloric acid	10	ccm
Water	3500	ccm

Allow the gelatine to soak in the water, add the salts and acid, melt at 60° C. (140° F.), and add:

Silver nitrate	500	g
Water	2000	ccm

Temperature 15° C. (60° F.). Add a few ccm of the silver solution to the salted gelatine and stir for one minute and then add the remainder in a fine stream in ten minutes. Raise the water bath to boiling and digest for thirty minutes, and add:

Gelatine	375	g
Water	3000	ccm

The gelatine should be soaked in the water and then the two added to the emulsion. Remove the crock from the water bath, or else run cold water round it as rapidly as possible, keep the emulsion stirred till the gelatine has dissolved, and continue stirring till it thickens, then put in ice room.

FAST NEGATIVE.—

Ammonium bromide	625	g
Potassium iodide	25	g
Gelatine	50	g
Hydrochloric acid	5	ccm
Water	2500	ccm

Temperature 60° C. (140° F.). Add as above:

Silver nitrate	500	g
Water	1750	ccm

Boil for seventy-five minutes.

Gelatine	450	g
Water	2000	ccm

Soak and melt at 40° C. (104° F.), add to the emulsion and cool in running water as above, and set in ice.

Or the following may be used:

Ammonium bromide	450	g
Potassium iodide	12.5	g
Gelatine	50	g
Hydrochloric acid	10	ccm
Water	4000	ccm

Raise to 60° C. (140° F.) and add:

Silver nitrate	250	g
Water	1000	ccm

Temperature 20° C. (68° F.). Boil for sixty minutes and add:

Gelatine, dry	330	g

When dissolved, add:

Silver nitrate	250	g
Water	1000	ccm

Digest for four hours at 35° C. (95° F.), set and wash.

In the above processes the emulsion does not actually boil; its temperature ranges from 95° to 98° C. (203° to 208° F.). The trouble with most of these formulas is that the plates have rather a low gamma infinity and, while suitable for portraiture, are less suitable for ordinary work. For this reason a modification has become fairly general, in which the emulsions are boiled for a certain time and then cooled down and digested for a given time with ammonia. This method will be found to give not only faster plates but a higher gamma. For the beginner this method will be found somewhat easier for the production of higher speed emulsions.

MEDIUM SPEED EMULSION. —

Ammonium bromide	475	g
Potassium iodide	5	g
Gelatine	150	g
Hydrochloric acid	25	ccm
Water	4125	ccm

Temperature 60° C. (140° F.).

Silver nitrate	500	g
Water	2500	ccm

Temperature 25° C. (77° F.). Boil for two hours and add:

Gelatine, dry	825	g

When dissolved, cool down to 35° C. (95° F.) and add in a fine stream:

Ammonia	75	ccm
Water	425	ccm

Digest for four hours, set and wash. By increasing the iodide to 7.5 g and time of digestion at 35° C. to six hours, a faster emulsion is obtained.

All sorts of variations may be rung on these formulas and methods of mixing, but for experimental work one factor only should be varied in each experiment, otherwise one is in doubt, if a difference in result is obtained, as to which factor is responsible.

In the following formulas all the solutions are brought to the same temperatures and the bromides and silver run into the gelatine simultaneously, care being taken, as already advised, to keep the bromide in excess:

Potassium bromide	400 g
Potassium iodide	10.6 g
Hydrochloric acid	1 ccm
Water	2270 ccm

Temperature 50° C. (122° F.).

Silver nitrate	500 g
Water	2270 ccm

Temperature 50° C. (122° F.).

Soft gelatine	77 g
Water	1400 ccm

Mixing should take about thirty minutes. Raise the water bath to boiling and digest for two hours, then add:

Hard gelatine, dry	200 g

As soon as dissolved, cool down to 35° C. (95° F.) and add in a fine stream:

Ammonia	50 ccm
Water	150 ccm

Digest for two hours at 43° C. (108° F.), set and wash. After washing, add:

Hard gelatine, dry	454 g

It should be noted that in adding dry gelatine to an emulsion it should be fed in fairly slowly in small quantities; otherwise, especially if leaf gelatine be used, one may find a solid lump of gelatine that defies almost any amount of stirring.

AMMONIA METHODS. — It will be seen that one or two of the formulas call for a mix without ammonia, and this is added afterward, therefore they are classified in this section, as the temperature is never raised to the boiling point.

SLOW CONTRAST EMULSION, SUITABLE FOR PROCESS WORK: —

Potassium bromide	450 g
Potassium iodide	5 g
Gelatine	625 g
Water	4800 ccm

Temperature 45° C. (113° F.).

Silver nitrate	500 g
Water	1250 ccm
Ammonia	q. s.

Dissolve the silver, add enough ammonia to form a clear solution, and cool down to 20° C. (68° F.). This should be run into the bromized gelatine in fifteen minutes and the emulsion digested for fifteen to thirty minutes, then cooled with running water, set and washed.

Another excellent formula, originally suggested by Eder, which works with great freedom from fog and gives very high gamma infinity, is:

Potassium bromide	400 g
Potassium iodide	13.3 g
Hard gelatine	333 g
Water	4160 ccm

Temperature 50° C. (122° F.).

Silver nitrate	500 g
Water	2080 ccm

To this is added:

Citric acid	50 g
Water	2080 ccm

and finally:

Ammonia	q. s.

to form a clear solution. On the first addition of the ammonia, a thick curdy white precipitate is formed, which is soluble in excess of ammonia. The temperature of this solution should be 20° C. (68° F.). Time of mixing twenty to thirty minutes. Digest at 45° C. (113° F.) for fifteen to thirty minutes according to speed required.

Another emulsion of similar character can be obtained from the following:

Sodium bromide	400 g
Sodium iodide	13.5 g
Sodium sulphite, cryst.	1.25 g
Gelatine	675 g
Water	4800 ccm

Temperature 45° C. (113° F.).

Silver nitrate	500 g
Water	1200 ccm
Ammonia	q. s.

Temperature 20° C. (68° F.). Digest for one hour at 45° C. (113° F.), then cool to 27° C. (81° F.), digest for two hours, set and wash.

It will be noted that in the above formulas there is a comparatively high percentage of gelatine in the mix; this is to keep the grain fine. The last formula is the only one the author has met with in which the sodium halides are used, and in which sulphite is present. This was communicated by an old emulsion maker, who considered that by this method a finer grain was obtained than by any other process, and although he always contended that he had discovered this himself, sufficient evidence was at intervals elicited from him so that the actual origin of the use of the sulphite was traced to Valenta's suggestion for its employment in Lippmann emulsions (see p. 131). This formula was repeatedly tested by the writer, and while no extra fineness of grain could be detected, it certainly gave very clean plates with high gamma infinity.

As a still greater curiosity may be mentioned an axiom promulgated by the same operator, who by the bye was not a chemist, that reversal of the direction of stirring of an emulsion during the mix inevitably produced fog, a statement that has, of course, about as much truth in it as that the moon is made of green cheese.

Ordinary Emulsions. — Rather faster, the so-called ordinary, emulsions for landscape work can be made from the following:

Ammonium bromide	460	g
Potassium iodide	15	g
Gelatine	675	g
Alcohol	375	ccm
Water	5000	ccm

Temperature 45° C. (113° F.).

Silver nitrate	250	g
Ammonia	200	ccm
Water	1500	ccm

Temperature 20° C. (68° F.). Digest for one hour at 45° C. (113° F.), and add:

Silver nitrate	250	g
Water	1500	ccm

Temperature 45° C. (113° F.). Digest for one hour at the same temperature and add:

Gelatine	950	g

When dissolved, set and wash. To prepare the bromide solution soak the gelatine in the water for thirty minutes, add the salts, melt and then add the alcohol. Alcohol is frequently used in mixing ammoniacal emulsions to prevent coarse grain, particularly when the ratio of gelatine is reduced.

A rather faster emulsion can be obtained with:

Potassium bromide	400	g
Potassium iodide	30	g
Gelatine	100	g
Water	3250	ccm

Temperature 45° C. (113° F.). Add:

Silver nitrate	500 g
Water	1500 ccm
Ammonia	q. s.

Temperature 45° C. (113° F.). The emulsion thus formed should be poured into:

Gelatine	500 g
Water	1800 ccm

Soak and melt at 50° C. (122° F.). Cool down with running water, set and wash. After draining, add:

Gelatine, dry	450 g

When dissolved, add:

Alcohol	1140 ccm
Hydrobromic acid, 1% sol.	75 ccm
Chrome alum, 10% sol.	30 ccm

Make up to 15,000 g and filter.

A modification of the above is:

Potassium bromide	425 g
Potassium iodide	9.6 g
Hydrochloric acid	3.6 ccm
Gelatine	132 g
Water	4000 ccm

Temperature 55° C. (130° F.). Add:

Silver nitrate	500 g
Water	2500 ccm

Temperature 52° C. (125° F.). Raise the temperature to 70° C. (158° F.) in twenty minutes, and add:

Gelatine	350 g

When dissolved, cool to 43° C. (110° F.) and add:

Ammonia	120 ccm
Water	340 ccm

Digest for thirty minutes, set and wash, and add when melted and cooled to 50° C. (122° F.):

Gelatine	552 g

Then make the other additions as in the previous formula.

There is one method in which but a small excess of bromide is used, but an excess of chloride. This has always given a clean and fairly fast plate:

Potassium bromide	300 g
Potassium iodide	15 g
Ammonium chloride	100 g
Gelatine	250 g
Water	4250 ccm

Temperature 50° C. (122°F.). Add:

Silver nitrate	500 g
Water	2500 ccm
Ammonia	q. s.

Temperature 22° C. (72° F.). Digest for one hour at 45° C. (113° F.), then cool down to 27° C. (81° F.), digest for four hours and add:

Gelatine	335 g

Raise the temperature sufficiently to dissolve the gelatine and set.

ISOCHROMATIC OR ORTHOCHROMATIC EMULSIONS. — As is probably well known, the ordinary commercial isochromatic emulsions are prepared by the addition of erythrosin to the emulsion, and the best result, that is the most marked color-sensitivity, is obtained when the dye is present at the moment of mixing. Ammonia emulsions are most suitable for this process, as the insoluble tetra-iodofluorescein is precipitated by acids. The dye may be added to the bromized gelatine or to the silver solution; in the latter case there is first formed a deep red precipitate of silver erythrosinate, insoluble in water but readily soluble in ammonia, therefore an ammoniacal solution must be used. There is no practical difference in the results of these two methods of mixing. It has been accepted as an axiom that emulsions intended for orthochromatizing should contain little or no iodide (see p. 44); but the writer has not found that the presence of larger quantities of iodide is prejudicial; certainly as high as five per cent has been successfully used.

The best erythrosin is the extra-bluish, which is the tetra-iodofluoresceinate of potassium. This is sold under various names and also in various strengths or purity, so that unless insistence is laid on the pure dye the results may not be as expected. In order to purify the dye, the following plan may be adopted: make a three per cent solution of the dye in water and filter, then add dilute sulphuric acid till the whole of the tetra-iodo compound is precipitated and the solution colorless. Filter and wash the filter repeatedly with distilled water and dry the dye. Or dissolve in alcohol and water with cautious addition of ammonia.

The quantity of dye naturally varies with the ideas of the maker, but from 0.07 to 0.1 g per 100 g of dry silver nitrate may be considered general practice.

MEDIUM ISOCHROMATIC. —

Potassium bromide	500 g
Potassium iodide	11 g
Soft gelatine	500 g
Hard gelatine	250 g
Water	5000 ccm

Temperature 50° C. (122°F.).

Silver nitrate	500 g
Erythrosin	1.875 g
Ammonia	400 ccm
Water	1250 ccm

Dissolve the erythrosin in 50 ccm of water, add to the silver dissolved in the remainder of the water, and then add the ammonia. Cool to 25° C. (77° F.), add to the bromized gelatine in the usual way, digest for one hour at 50° C. (122° F.), set and wash.

RAPID ISOCHROMATIC. —

Ammonium bromide	380	g
Potassium iodide	15	g
Soft gelatine	135	g
Water	4800	ccm

Temperature 50° C. (122° F.).

Silver nitrate	500	g
Erythrosin	1.875	g
Ammonia	400	ccm
Water	1250	ccm

Temperature 40°C. (104° F.). Make this solution as above. Add one-fourth of this solution to the bromized gelatine and digest for thirty minutes, then add:

Hard gelatine	135	g

When dissolved, add half the remainder of the silver solution and digest for one hour at 40° C. (104° F.), then add:

Hard gelatine	480	g

When dissolved, add the remainder of the silver solution, digest for one hour and set.

As an alternative the dye may be added to the gelatine solution, and obviously any of the other ammonia formulas may also be used with the dye.

The following method, though never used by the author, has been in use for many years commercially:

Ammonium bromide	340 g
Gelatine	75 g
Water	3750 ccm

Temperature 35° C. (95° F.). Dissolve and add:

Silver nitrate	335 g
Ammonia	110 ccm
Water	760 ccm

Temperature 40° C. (104° F.). Time of mixing fifteen minutes. Then add:

Ammonium iodide	6.5 g
Ammonia	110 ccm

Temperature 20° C. (68° F.). Then add:

Silver nitrate	165 g
Water	380 ccm

Temperature 40° C. (104° F.). Time of mixing fifteen minutes. Add:

Hard gelatine, dry	455 g

Allow to soak for ten minutes in the emulsion, raise to 46° C. (115° F.) and stir till the gelatine is dissolved, then set and wash next day for thirty minutes with water at 15° C. (50° F.). Allow the worms to drain for ten minutes, when the weight should be 9000 g. Melt at 35° C. (95° F.) and add:

Hard gelatine, dry	570 g

Raise to 46° C. (115° F.) to dissolve the gelatine, then cool to 35° C. (95° F.) and add:

Erythrosin	0.5 g
Ammonia	50 ccm

Digest from twelve to sixteen hours at 33° C. (92° F.). Set and wash for one hour, or till free from ammonia. Add:

Alcohol	900 ccm

Melt and make the total bulk to 15,000 g.

A modification of the above was to add the iodide to the bromized gelatine and add the ammoniacal dye solution instead of the iodide, that is just before the last lot of silver solution.

For self-screened or non-filter plates add, just before coating, a yellow dye, such as 0.16 per cent of naphthol yellow S, or 0.075 per cent of tartrazin or filter yellow, or 0.1 to 0.2 per cent of thiazol yellow, nitrophenin or canary yellow.

Recently a new dye has been introduced by Meister, Lucius & Brüning, of Höchst, under the name of pinaflavol, which would seem to possess marked and distinctly advantageous properties as a color sensitizer. This is a basic dye of a new class and sensitizes up to the D lines, wave-length 5893, with a maximum at E, wave-length 5270, joining on to the individual sensitiveness of bromo-iodide of silver, without the marked gap between b and F given by erythrosin and other eosin dyes. No report has been made of the suitable strength for gelatine emulsions, but for collodion 0.02 to 1000 of collodion emulsion is advised.[1]

W. H. Mills & J. W. Pope[2] described the preparation of 2-p-dimethylaminostyrylpyridin methiodide from α-picolin ethiodide, p-dimethylaminobenzaldehyde and piperidine. This is obtained in bright red prisms with blue reflex, giving an orange colored solution that shows absorption bands at about 4750 and 4600. Plates bathed in 1 : 30,000 to 40,000 solution showed almost uniform sensitiveness to all wave-lengths from the blue to 5600, there being no gap in the blue-green. This is probably the same as or closely allied to pinaflavol.

Panchromatic Plates. — For making panchromatic emulsions the best dyes to use are orthochrom T or sensitol green and sensitol violet (pinachrom violet), and these dyes should be added to the emulsion just before coating. It should be noted that the emulsions must not be acid. The dye solutions should be mixed with the alcohol usually employed and added with constant stirring to the fluid filtered emulsion. About 20 ccm of sensitol green solution, 1: 1000 alcohol, and 10 ccm sensitol violet, same strength, should be added to every liter of emulsion.

Fast Emulsions. — Of all problems in photography that of making a really fast clean-working emulsion with a decently high gamma infinity is about the hardest. Speed may be obtained but with too much fog; reduce the latter to reasonable limits and down goes the speed in the most unaccountable fashion. There is, on the other hand, one fact that stands out pretty prominently and that is, the moment bad fog sets in the speed begins to drop and in an incredibly short time.

The secret of a fast emulsion lies in the very first stage of the mix. If one starts with a slow form of silver halide, there seems to be no possible means of making that emulsion fast. Exactly what the secret is may be known, but it is doubtful. One of the factors at any rate is reduction of the quantity of gelatine, obviously reducing the protecting action of the colloid. Naturally there is a limit below which it is unsafe to go, otherwise a coarse granular silver salt is formed and thin results are obtained; there must be enough gelatine to carry the halide, and a common trick is to add more gelatine as emulsification proceeds. One has, of course, always the possible assistance of the use of alcohol against coarse grain, a matter which is dealt with elsewhere (see p. 62).

The digestion for speed may be effected all at once at a comparatively high temperature, or spread over a longer time at a lower temperature, as in the following formula:

Ammonium bromide	475	g
Potassium bromide	10	g
Soft gelatine	100	g
Water	1125	ccm

Temperature 50° C. (122° F.). Add in an eighth inch stream:

Silver nitrate	125 g
Ammonia	125 ccm
Water	300 ccm

Temperature 50° C. (122° F.). As soon as mixed, take a dip test and, if the color is reddish, digest for ten minutes or till the dip test is distinctly orange. Then add:

Silver nitrate, dry	375 g

Digest at 43° C. (110° F.) for two hours, then lower to 38° C. (100° F.), digest one and a half hours and set in ice, and leave sixteen hours. Then melt to 48° C. (118° F.) and add:

Hard gelatine	625 g

This should have been washed for an hour, drained for an hour and melted at 48° C. (118° F.). Cool the whole in running water, set in ice and wash next day. This should make 25,250 g.

The dip test mentioned is one that is often followed, and while it is not always a sure sign it is by no means a bad guide. When first mixed with any reasonable quantity of gelatine, a drop or two of emulsion put on a sheet of glass and examined by a gaslight appears a perfectly transparent blood-red color, without the slightest sign of grain. As the digestion proceeds, the color changes to orange and then through green to blue, and at this stage the digestion should be stopped. If the color reaches a greyish-violet the emulsion nearly always shows fog.

The following formula is peculiar in that a rather high ratio of iodide is used and the plates take rather longer to give a certain gamma:

Ammonium bromide	500	g
Potassium iodide	50	g
Soft gelatine	200	g
Water	5680	ccm

Temperature 50° C. (122° F.). Add:

Silver nitrate	450	g
Water	2340	ccm
Ammonia		q. s.

Temperature 22° C. (72° F.). Time of mixing thirty minutes. Digest at 50° C. (122° F.) for fifteen minutes and add:

Silver nitrate	50	g
Water	450	ccm
Nitric acid	27.5	ccm

Digest for two hours at 50° C. (122° F.) and add:

Gelatine	1000	g

which has been previously washed for thirty minutes and melted. Then add:

Ammonium bromide	55	g

The following is on the same lines as one previously given for a slower emulsion:

Ammonium bromide	510	g
Potassium iodide	15	g
Soft gelatine	120	g
Hydrochloric acid	1	ccm
Water	2500	ccm

Temperature 60° C. (140° F.). Add:

Silver nitrate	500	g
Water	2500	ccm

Temperature 60° C. (140° F.). Time of mixing thirty minutes. Boil for one and a half hours and add:

Hard gelatine	400	g

Cool down to 35° C. (95° F.) and add:

Ammonia	50	ccm
Water	150	ccm

Digest four hours at 27° C. (80° F.).

The following method in which digestion is made with only part of the silver is also worthy of attention:

Ammonium bromide	500	g
Potassium iodide	15	g
Soft gelatine	100	g
Alcohol	100	ccm
Water	1000	ccm

Temperature 40° C. (104° F.). Then add:

Silver nitrate	250	g
Water	1250	ccm
Ammonia		q. s.

Digest at 50° C. (122° F.) for one hour and add:

Hard gelatine	200	g

When dissolved, add:

Silver nitrate	250	g
Water	1250	ccm
Ammonia		q. s.

Digest four hours at 32° C. (90° F.) and add:

Hard gelatine	500	g

Raise the temperature till the gelatine melts, then cool down in running water and set on ice.

A variation of this gives rather a higher gamma infinity, that is to add only one fourth of the silver the first time and the remainder afterwards.

The following also gives a fast emulsion, but is rather time-consuming:

Ammonium bromide	410	g
Potassium iodide	8	g
Soft gelatine	120	g
Water	4000	ccm

Temperature 44° C. (112° F.). Add:

Silver nitrate	450	g
Water	2000	ccm
Ammonia		q. s.

Digest for thirty minutes at 50° C. (122° F.), and add:

Hard gelatine	280	g

When dissolved, add:

Silver nitrate, dry	50 g

Digest one and a half hours at 50° C. (122° F.). Cool down in running water and allow to stand in water at 10° C. (50° F.) for forty hours. Melt to 50° C. (122° F.) and add:

Hard gelatine	175 g

Digest for forty-five minutes, cool down in running water for sixty minutes and allow to stand in water at 10° C. (50° F.) twenty-four hours, then wash.

In the following the quantity of ammonia is kept comparatively low, and ammonium nitrate is used with excellent results:

Ammonium bromide	410	g
Potassium iodide	8	g
Gelatine	80	g
Ammonium nitrate	250	g
Water	4000	ccm

Temperature 50° C. (122° F.). Add:

Silver nitrate	100	g
Water	500	ccm
Ammonia		q. s.

Temperature 25° C. (77° F.). Digest for thirty minutes at 50° C. (122° F.) and add:

Gelatine	200 g

As soon as dissolved add:

Silver nitrate	400	g
Water	2000	ccm

Temperature 25° C. (77° F.). Digest four hours at 32° C. (90° F.), and add:

Gelatine	500	g

Raise the temperature to 38° C. (100° F.) and stir till the gelatine is dissolved, then cool to 32° C. (90° F.) and digest one to two hours. Set.

One of the most unique methods, which is employed commercially, is the following:

Soft gelatine	75	g
Ammonia	90	ccm
Alcohol	100	ccm
Water	800	ccm

Dissolve at 50° C. (122° F.) and add simultaneously, keeping the bromide in excess:

Ammonium bromide	375	g
Potassium iodide	40	g
Water	2000	ccm

and:

Silver nitrate	500	g
Water	2000	ccm

Both these solutions should be at 21° C. (70° F.). Time of mixing thirty minutes. Digest for thirty minutes and add:

Gelatine	225	g

Set and wash. Next day, melt and add:

Gelatine	450 g

Keep the emulsion at a temperature of 33° C. (92° F.) for from eight to ten days, taking a test every day after the sixth day. When fast enough, raise the temperature to 50° C. (122° F.) and add:

Gelatine	225 g

When dissolved, filter and coat. In this case there is ripening of the washed emulsion, and there is no question as to the excellent results obtained, as the writer has actually tested on successive days trial plates of such an emulsion.

Some workers hold the opinion that far cleaner emulsions can be obtained with no sacrifice of speed by adding the ammonia to the bromized gelatine, in preference to the formation of the ammonio-nitrate of silver, and in this case, as there is less ammonia used, there may be less chance of fog. In both cases the silver halide is formed in the presence of ammonia, therefore the initial speed is greater than when an acid mix is used. Others again pin their faith to the ammonio-carbonate of silver, holding this to be less prone to fog formation. For comparatively slow emulsions this method is satisfactory, though in the writer's hands it has never given really fast emulsions. On the addition of ammonium carbonate to silver nitrate there is first formed a yellow precipitate of silver carbonate, which is soluble in excess of carbonate or in ammonia solution. A typical formula for this is:

Silver nitrate	250 g
Water	625 ccm

When dissolved, add:

Ammonium carbonate	50 g
Water	625 ccm

Then add:

Ammonia	q. s.

Temperature 50° C. (122° F.). Now make up:

Ammonium bromide	350 g
Potassium iodide	16.5 g
Gelatine	32 g
Water	2500 ccm

Temperature 50° C. (122° F.). Add the silver solution and after five minutes add:

Silver nitrate	250 g
Water	1250 ccm

Then immediately stir in:

Hard gelatine	680 g

Digest at 48° C. (118° F.) for two hours and set and wash. Melt to 50° C. (122° F.) and add:

Hard gelatine	1135 g

Digest four hours, then add:

Alcohol	1000 ccm
Chrome alum	10 g

The total bulk should weigh 11,000 g. This was specially intended for film and should coat six hundred square feet of celluloid.

In almost every case an improvement will be obtained by subsequent digestion. That is to say, after the emulsion has been washed, there is generally an increase in speed and also in gamma. This after-digestion may vary considerably, from one to two hours to days. The digestion temperature should, however, be somewhat low, the most favorable having been found to be 35° C. (95° F.).

Some workers prefer to redigest for say four hours, reset and chill and again redigest for another period, claiming that this resetting and remelting acts more favorably than continuous heating. Probably if there is any improvement by this method, and it has not been confirmed by the writer, it may be due to the fact that rather higher temperatures are actually required to remelt each time.

It will be noted that in some of the formulas given above, the whole of the gelatine is added to the emulsion before shredding and washing. When complete control over the temperature of the washing waters is possible this procedure is allowable. On the other hand, it leads to considerable increase in the time of washing, in consequence of the emulsion being harder. It also leads to an increase in the total bulk, in consequence of more water being picked up. This, in certain cases, for film work for instance, is a great disadvantage. It is as well, therefore, to hold back some of the gelatine in every case, and add this to the washed emulsion. This reduces the total bulk and gives a dried film which is harder and less liable to troubles in hot weather.

SETTING THE EMULSION. — It will be obvious on a little consideration that the method of setting an emulsion may play considerable part in the ripening process. For instance, assuming that one has a total bulk of 7,000 ccm of emulsion in a crock and this is cooled down by cold water, it will be some time, possibly twenty to thirty minutes, before it becomes too viscous to stir, and still longer before the center of the mass has become quite cold, even when placed in ice water, so that during the whole of this time the ripening will be going on. If, on the other hand, the emulsion be poured out into an ice-cold dish to the depth of a few centimeters, there is not only the chilling of the larger area in the dish, but also the surface is exposed to the air, thus the whole of the emulsion will be chilled in about one-fourth of the time of the crock method. The difference in speed may be as much as one hundred per cent with the ammonia process. One should also take into consideration in these two methods that in the one case, with the crock, the escape of ammonia is practically nil, while with the open pan method the ammonia is escaping all the time.

Then it is possible, particularly with those emulsions in which a lesser quantity of ammonia is used, to continue the ripening by allowing it to stand longer in the ice room. This does not give so much increase in speed as increase of gamma infinity.

There is, however, a possibility, when larger quantities of ammonia are used, of greater increase of fog without commensurate gain in other respects.

Acid emulsions do not tend to so great an increase in speed by standing in the cold; but those which are subsequently mixed with ammonia do ripen considerably, and also give higher gammas.

The concentration of the gelatine has also considerable influence on the ripening and, probably on account of its action as a protective colloid, the higher the gelatine content as a rule the less the ripening, and certainly the less the increase in fog.

It is impossible to lay down any hard and fast rules as to the after-ripening of unwashed emulsions, because of the great variations in gelatine, ammonia and silver halide content and the temperature at which emulsions are kept. Storing the crocks, for instance, in cold water, which may mean any temperature from 4° to 10° C. (39° to 50° F.), will naturally cause marked differences in results.

Some manufacturers only digest for a short time at a high temperature and rely upon a prolonged digestion at a very much lower one, when the emulsion is in a firm gel and yet not ice-cold. In one case, with an emulsion with full ammonia content, digestion was carried for thirty minutes only at 50° C. (122° F.) with an after-digestion at 32° C. (90° F.) for three days, with excellent results. While this method gives good results, it entails considerable time and it is essential to still further chill the emulsion before washing, otherwise the worms pick up far too much water, with a sloppy result. It is in fact five days before the emulsion can be ready for the coating machine.

NON-HALATION PLATES. — The ordinary method of preventing halation is, of course, by coating the back of the glass with a non-actinic color; but this necessitates the handling of the coated plate, with possible chance of damaging the film of emulsion. It is also obvious that if the light could be prevented from penetrating right through the emulsion and glass there would be no halation. O. Magerstadt[3] patented the use of a preliminary coating of gelatine stained with a non-actinic dye, fuchsin being actually used. C. E. Pettit[4] also patented the same idea. Any acid red dye may be thus used, or a mixture of red and yellow dyes. Acid dyes must be used for this purpose, as they are more readily washed out of the gelatine. Only a thin coating of the stained gelatine is required, a five per cent solution being sufficient.

If the dyes do not readily wash out, they must be of such a nature as to be decolorized either by acid sulphite or other ready means, otherwise they would seriously prolong the exposure in printing. Congo red has been used, and probably carmine L, lanafuchsin SB, or tolan red with or without a yellow admixture, such as naphthol yellow or tartrazin, could be used.

With the idea that the use of dyes might lead to trouble because of partial sensitizing or fogging action by diffusion into the emulsion layer, C. F.

Oakley[5] patented the use of a 0.6 per cent solution of potassium permanganate in gelatine. The permanganate is reduced to practically colloidal manganese hydroxide, which has in this state an orange-brown color, that is very intense and can not diffuse into the emulsion. It has the further advantage of being readily soluble in the ordinary acid fixing bath, or may be removed by sodium bisulphite. Further than that, it is obvious that it forms a better protection for panchromatic emulsions.

Some of the non-halation, so-called double-coated plates, on the market are merely coated with an extra quantity of emulsion, and not actually double-coated, using this term in the original sense, employed by J. T. Sandell,[6] who actually coated first a very slow, opaque emulsion and then on top a faster and more translucent one. The disadvantage of these extra thick coatings is the longer time required for fixation, washing and drying.

[1] *Phot. Rund.*, 1921, **57**, 80; *Brit. J. Phot.*, 1921, **68**, *Col. Phot. Supp.* **14**, 16; abst. *Sci. Tech. Ind. Phot.*, 1921, **1**, 37; *J. S. C. I.*, 1921, **40**, 324 A; *Amer. Phot.*, 1922, **16**, 119; *D. R. P.* 395, 666.

[2] *J. C. S.*, 1922, **121**, 946; abst. *Sci. Tech. Ind. Phot.*, 1922, **2**, 86; *Amer. Phot.* 1922, **16**, 727.

[3] *Eng. Pat.*, 5,932, 1893.

[4] *Eng. Pat.*, 8,956, 1893.

[5] *Eng. Pat.*, 2,986, 1895.

[6] *Eng. Pat.*, 21,381, 1891.

CHAPTER V

SPECIAL TYPES OF EMULSIONS

FILM EMULSIONS. — One would naturally assume that film emulsions would not differ from ordinary plate emulsions, and as regards cut sheet films, these may be used if the film is coated on the flat. But for cinematographic and camera work they do differ, mainly because of the different method of coating.

For positive work, the requirements for the emulsion are, a high gamma infinity, with perfect freedom from fog and high velocity constant. For negative emulsions, almost the same conditions are required, though such a high gamma is not essential. These requirements have been set by the operators in cinematographic laboratories, who, in the early days at least, felt it imperative to have a negative emulsion which they could "punch," so as to get as much out of the film as possible; totally regardless of the fact that a developer cannot bring out more than the light action has put in. In positive work, the operators required an emulsion that would give good "guts," by which they meant somewhat hard contrasty pictures, which actually, when projected, looked harsh on the screen, for the contrasts always appear increased in projection.

Fortunately a more sane view of matters now prevails, and one can see pictures which have good details in the highlights without blocked-up shadows. Of course, a good deal of the trouble was due to the economy (?) of using a developer over and over again till it was loaded with bromide, without making a corresponding allowance in the exposure and duration of development. But this is not a treatise on the development and printing of cinematographic film.

A good positive emulsion can be made on the following lines:

Potassium bromide	460 g
Potassium iodide	1.04 g
Hydrochloric acid	3.5 ccm
Water	3000 ccm

Temperature 50° C. (122° F.).

Silver nitrate	500 g
Water	3000 ccm

Temperature 50° C. (122° F.).

Gelatine	150 g
Water	1200 ccm

Temperature 50° C. (122° F.). Run the bromide and the silver into the gelatine solution simultaneously, keeping the bromide in excess. As soon as mixed add:

Ammonia	60 ccm

Digest for one hour at 43° C. (110° F.), and add:

Gelatine, dry	730 g

As soon as dissolved, set and wash. Melt after draining in the usual way, and add:

Gelatine, dry	230 g
Alcohol	650 ccm
Chrome alum	4 g

Make the total bulk to 12,500 g.

Again, the following may be adopted:

Potassium bromide	460 g
Potassium iodide	2.5 g
Hydrochloric acid	3.5 ccm
Water	4520 ccm
Gelatine	130 g

Temperature 55° C. (131° F.). Add in a fine stream:

Silver nitrate	500 g
Water	2500 ccm

Temperature as above. Digest for thirty minutes, and add:

Gelatine	550 g

When dissolved, cool to 35° C. (95° F.), and add:

Ammonia	60 ccm

Set and wash, drain and melt to 50° C. (122° F.), and add:

Gelatine	276 g

When dissolved, add:

Alcohol	800 ccm
Chrome alum	9 g

Make the total bulk to 12,500 g.

The ratio of iodide may be varied within reasonable limits, and it is a curious fact that with greater quantities the emulsion becomes distinctly red-sensitive. The quantity of gelatine may also be varied to suit the coating, but eight to nine per cent of the final bulk is the normal quantity.

For a negative emulsion, one may use:

Ammonium bromide	510 g
Potassium iodide	1.7 g
Gelatine	75 g
Water	3750 ccm

Temperature 35° C. (95° F.) Add:

Silver nitrate	500 g
Water	750 ccm
Ammonia	165 ccm

Temperature 18° C. (65° F.). Digest for ten minutes, and add:

Erythrosin	0.8 g
Alcohol	10 ccm
Water	100 ccm

Then add:

Silver nitrate	250 g
Water	380 ccm

Temperature 18° C. (65° F.). Add:

Gelatine, dry	500 g

When dissolved, cool to 35° C. (95° F.), and add:

Ammonia	75 ccm

Digest at 32° C. (90° F.) for six to ten hours, set, wash, drain and melt to 35° C. (95° F.), and add:

Alcohol	1140 ccm
Chrome alum	10 g

Make total bulk to 15,000 g. The erythrosin may be omitted if desired.

Transparency Emulsions. — Under this term are included the faster, essentially silver bromide emulsions, intended for lantern slide or transparency making, either by contact or copying in the camera. These are more used for black or warm brown tones, and can be made either by the acid or ammonia process. They are either pure bromide or have small iodide content.

A.	Ammonium bromide	335 g
	Potassium iodide	8 g
	Gelatine	750 g
	Hydrochloric acid	7.5 ccm
	Water	7500 ccm
B.	Silver nitrate	500 g
	Water	2750 ccm

Raise both solutions to 43° C. (110° F.), run B slowly into A, and digest for two hours at the same temperature. Set and wash.

A.	Potassium bromide	415	g
	Potassium iodide	2.5	g
	Gelatine	160	g
	Water	3750	ccm
B.	Silver nitrate	500	g
	Water	1250	ccm

Raise both solutions to 43° C. (110° F.), and run B slowly into A. Digest for one and a half hours at above temperature, and add:

Gelatine, dry	750	g

Stir till dissolved, and add:

Ammonia, sp. gr. 0.90	50	ccm
Water	450	ccm

Set immediately.

A.	Sodium bromide	463	g
	Potassium iodide	5	g
	Gelatine	725	g
	Water	5000	ccm
B.	Silver nitrate	250	g
	Ammonia		q. s.
	Water	750	ccm
C.	Silver nitrate	250	g
	Water	750	ccm

Raise A to 43° C. (110° F.) and add B, which must be cooled to 18° C. (65° F.). After five minutes, add C also at 18° C. and immediately set. In this formula the ammoniacal silver solution may be added very rapidly, that is in about one minute, as there is no fear of a coarse grain, and C may be added in the same way.

A pure bromide lantern emulsion can be made as follows, and for years lantern plates of this type were much in favor in England, as almost any color can be obtained by suitable variation of the exposure and developer:

Ammonium bromide	312	g
Citric acid	5	g
Soft gelatine	122	g
Water	4440	ccm

Temperature 60° C. (140° F.). Add:

Silver nitrate	500	g
Water	4440	ccm

Temperature 60° C. (140° F.). Mix in twenty minutes, then add:

Hard gelatine	1330	g

This should have been previously soaked in water for one hour and drained one hour. As soon as this has dissolved, set and wash as usual. This should make 33,300 ccm for coating.

CHLORIDE EMULSIONS. — The great advantage of the chloride and bromo-chloride emulsions is the ease with which warm tones can be obtained, and the extremely fine-grained image that they give, which is more like a stain than the normal silver image. They are specially suitable for lantern slide and transparency work and for the reproduction of line diagrams and black and white work.

The emulsions are easy to make, except that they are, under certain conditions, particularly liable to the formation of a characteristic coarse grain, technically known as " pepper," which is distributed throughout the emulsion and is reduced to the metallic state without exposure to light. This is sometimes so fine that it cannot be seen by mere visual examination, therefore, test plates should always be examined with an eyepiece, particularly in those parts protected from light action.

There are two methods which may be adopted in the mixing of the emulsions to avoid this grain. One is to reduce the quantity of water during the mix, and the other to add the silver nitrate dry to the chlorized gelatine and stir till thoroughly dissolved.

There can be with these, as with negative emulsions, a ripening process, but usually a comparatively slow emulsion is desired. Any chloride can be used, but ammonium chloride will satisfy all needs, though there is little difference in the results if the equivalent weights are used. But the ammonium salt can always be obtained pure and it is one of the cheapest chlorides.

Ammonium chloride	275 g
Hydrochloric acid	12.5 ccm
Gelatine	1225 g
Water	7500 ccm

Soak the gelatine in the water for thirty minutes, add the acid and the salt and raise the temperature to 50° C. (122° F.). Add in a fine stream:

Silver nitrate	500	g
Water	1200	ccm

Stir vigorously all the time. The silver solution should be at room temperature. Allow the emulsion to digest for thirty minutes at 44° C. (112° F.) with continual stirring, then set and wash.

The method with the dry silver nitrate is very similar:

Ammonium chloride	275	g
Hydrochloric acid	12.5	ccm
Gelatine	1670	g
Water	15000	ccm

Heat to 44° C. (112° F.) and add:

Silver nitrate, dry	500	g

Maintain the temperature for thirty minutes and set.

The following formula gives an emulsion which has considerably more contrast, and with which it is still easier to obtain warm tones:

Ammonium chloride	225	g
Citric acid	225	g
Cupric chloride	7.5	g
Gelatine	1650	g
Water	8300	ccm

Allow the gelatine to soak, add the salts and the acid, and heat to 44° C. (112° F.). Then add:

Silver nitrate	500	g
Water	5000	ccm

Digest at above temperature with continuous stirring for thirty minutes, then set.

These emulsions should be shredded as usual and washed for about three hours and then melted at 44° C. (112° F.), and the following added:

Gelatine	900	g
Alcohol	2500	ccm
Basic chrome alum sol.	100	ccm
Hydrochloric acid	5	ccm
Water to make	45000	ccm

The action of the cupric chloride is to increase contrast and the quantity may be varied at will.

A fast chloride emulsion may be made by using the first formula given above, and after mixing raising the temperature to 55° C. (122° F.) and digesting for sixty minutes, but if a still faster emulsion is required it is much better to adopt one of the chloro-bromide formulas, as there is less danger of fog.

The slow chloride emulsions given above may be considered to be practically of the same type as the slow gaslight lantern plates on the market.

CHLORO-BROMIDE AND BROMO-CHLORIDE EMULSIONS. — It is usual to differentiate between these two in the above way, and the first term signifies that silver chloride is in excess, the latter that the bromide predominates. The ratio between the two varies according to the ideas of the maker and the type of the emulsion desired. The more bromide an emulsion contains in comparison to the chloride, the faster it is, as a rule, the longer the scale of gradation and the less easy to obtain warm tones.

Some misconception exists generally, though not in the minds of expert emulsion makers, as to the cause of the warm tones, and it is stated that the duration of the exposure and also the content of the chloride have considerable influence on the resultant color. For instance, Eder [1] says in speaking of these emulsions: "The exposure is, however, more certain with a gas burner, for instance, with an incandescent gaslight at half a meter distance, from ten seconds to one minute; other light-sources, such as magnesium ribbon, which are richer in the violet rays than ordinary gaslight, effect to a greater degree the silver chloride contained in chloro-bromide plates and produce a photo-chemical effect and impart to the finished developed images more of those warm tones which are more characteristic of silver chloride than of silver bromide. These differences, however, are only striking when the films are rich in silver chloride."

In order to settle this point, some experiments were made by the author [2] in which a series of emulsions was made, starting with a pure chloride of silver and then with increasing percentages of bromide from five, ten, twenty, etc., to a pure bromide emulsion. The plates were exposed under a test plate of varying densities from 1 to 3.01, that gave exposures from 1 to 1024. The exposures were made to magnesium ribbon, a Nernst lamp and incandescent gas, and a constant developer, metol-hydrochinon, was used. In every case the same colored image was obtained from the lightest to the deepest deposit, which conclusively proved that the length of exposure with a constant developer has nothing to do with the color of the image. In further experiments with a weaker developer and increased bromide content, warmer tones were obtained, but they were the same on all plates, thus proving that it is the rate of development, or in other words, the rate of deposition of the silver which is the determining factor of the color of the image, and not the composition of the emulsion. Chapman Jones[3] has also proved that the color of the image is dependent on the size of the silver particles. Were the color dependent on the exposure, everyday practice in the making of transparencies from negatives would prove this, because in exposing a plate under a negative it is obvious that varying exposures must be given in the ratio of the opacities of the negative image, possibly not to such a degree as in the above mentioned test plate, but in an ordinary normal negative the densities may easily vary from 1 to 2.5.

The speed of the chloro-bromide emulsions and their contrast being dependent on the bromide content, it is clear that various emulsions can be easily prepared to answer every requirement. By the use of the tables given on p. 256 it is possible to so apportion the ratios of the alkaline halides as to produce any desired composition. According to Valenta,[4] who analyzed several commercial plates of this type, the ratio of chloride to bromide varies considerably, from 50: 50 in the German plates to 15: 85 in the English. The ratio of gelatine to the silver halides varied from 2: 1 to 6: 1 in the English plates.

The following formulas are given because they have been proved commercially to be reliable. The first two were given by Valenta, the third by Wellington, the fourth by S. H. Wratten, and the fifth is that of a commercial plate which was a great favorite in England.

I. Valenta's. Ratio of chloride to bromide, 100 to 133.67:

A.	Ammonium chloride	25	g
	Ammonium bromide	255	g
	Nitric acid	5	ccm
	Gelatine	830	g
	Water	6665	ccm
B.	Silver nitrate	500	g
	Water	6665	ccm

II. Valenta's. Ratio of chloride to bromide 100: 13.275. This is suitable for thin flat negatives and gives greater contrasts from normal negatives:

A.	Ammonium bromide	26	g
	Ammonium chloride	150	g
	Nitric acid	5	ccm
	Gelatine	830	g
	Water	6665	ccm
B.	Silver nitrate	500	g
	Water	6665	ccm

Allow the gelatine to soak in the water, add the salts and acid. Raise the temperature to 50° to 60° C. (122° to 140° F.), and after heating the silver to the same degree add to the salted gelatine with constant stirring.

III. Wellington's. Ratio of chloride to bromide 100: 173.97. Gives very warm tones with suitable developer:

A.	Ammonium bromide	200 g
	Sodium chloride	100 g
	Citric acid	500 g
	Gelatine	700 g
	Water	5000 ccm
B.	Silver nitrate	500 g
	Citric acid	500 g
	Water	5000 ccm

Soak the gelatine, add the salts and acid, heat to 70° C. (158° F.) and add the silver solution cold, allow to stand for ten minutes, then set.

IV. Wratten's. Ratio of chloride to bromide 100: 357.64 This gives a very long scale of gradation:

Soft gelatine	1000 g

Rinse two or three times in distilled water and add to:

Water	4280 ccm

Dissolve by heat and add:

Ammonium bromide, neutral	275 g
Sodium chloride	150 g
Hydrochloric acid	2.5 ccm

Heat to 52° C. (125° F.) and add in a fine stream:

Silver nitrate	500 g
Water	1100 ccm

Digest for ten minutes at 65° C. (150° F.) and add:

Hard gelatine	437 g

which has been previously soaked in water for about thirty minutes, and as much water as possible drained off. As soon as the gelatine has melted, set in ice. Subsequently shred, wash for thirty minutes in six changes of water, drain well, melt, make total bulk to 8750 ccm, and add:

Tannin	5.15 g

V. Commercial rapid chloride. Ratio of chloride to bromide 100: 91.75. Fairly fast emulsion readily giving black tones in preference to warmer ones:

A.	Potassium bromide	192.5 g
	Sodium chloride	265 g
	Gelatine	500 g
	Hydrochloric acid	2.5 ccm
	Water	5000 ccm
B.	Silver nitrate	500 g
	Water	5000 ccm
C.	Gelatine	500 g
	Water	5000 ccm

Soak the gelatine in the water and add the salts in A and heat to 55° C. (131° F.). Heat B and C to the same temperature and add B to C, and run this silver-gelatine into A in a fine stream with continual stirring. This should take two hours to mix. Digest for sixty minutes at the above temperature, and add:

Gelatine	500 g

When dissolved, set and wash. Frequently in mixing this, coarse flocks of silver halide form at first, but with continued digestion and stirring these entirely disappear.

It will be noted that in Wellington's formula there is a large quantity of citric acid; this tends to the production of warm tones. Wratten advises the addition of tannin as a hardening agent and this is very effective; but it must be used with caution, as it tends to give a yellow stain during development, if used in too large a quantity. The ratio advised is 1 of tannin to 286 of gelatine.

[1] *Handbuch*, 1905, **3**, 725.

[2] *Jahrbuch*, 1911, **25**, 39.

[3] *Phot. J.*, 1911, **51**, 159.

[4] *Jahrbuch*, 1900, **14**, 605.

CHAPTER VI

PRINTING PAPER EMULSIONS

GELATINE EMULSIONS. — Gelatine emulsions for paper may be divided into pure bromide and mixtures of bromide and chloride, the former being intended for black images, and the latter for the development or gaslight type. The former are, as a rule, more rapid than the latter, and are always washed emulsions, the gaslight being usually unwashed. In both cases there is less gelatine used, as a rule, than with plate emulsions.

Any of the transparency emulsions already given may be used with slight alteration, but the following have been actually employed commercially and are given as typical.

BROMIDE PAPER EMULSIONS. —

Potassium bromide	400	g
Citric acid	400	g
Gelatine	150	g
Water	1800	ccm

Soak the gelatine in the solution of the salts and melt at about 50° C. (122° F.), then cool to 30° C. (86° F.) and add:

Silver nitrate	500	g
Water	3750	ccm
Ammonia		q. s.

Temperature of mixing 30° C. (86° F.). As soon as mixed, pour into:

Gelatine	150 g
Water	600 ccm

Raise to 50° C. (122° F.) and as soon as the gelatine has melted, set. After washing, melt to 40° C. (104° F.) and add:

Gelatine	454 g
Water	1600 ccm

previously soaked and melted. Then add:

Alcohol	568 ccm
Chrome alum, 10% solution	30 ccm

The total bulk should be 11,400 g.

In some cases a very small proportion of iodide is used, about 0.5 to 1.0 per cent. The quantity of gelatine naturally varies with the surface desired, whether glossy, half-matt, etc. In the above formula it is approximately 1: 15. For obtaining a real matt surface, various additions have been made, such as tripoli, kieselguhr (infusorial earth) and starch. The latter, rice starch, is quite satisfactory, and the method of mixing is given on p. 157. In order to obtain half-matt surfaces, the starch should be boiled in water till a transparent paste is formed, cooled down and then added to the emulsion before filtering.

As bromide emulsions are always slow, it is sometimes the custom to pour them out, immediately after digestion or mixing, into ice-cold pans to the depth of about an inch or so, in order that they may set quickly and thus stop the ripening. For enlarging paper it is usual to make a more rapid emulsion, which can easily be done by a more or less brief digestion.

GASLIGHT OR DEVELOPMENT PAPERS. — These are as a rule unwashed emulsions containing varying ratios of bromide and chloride of silver. The remarks on varying the ratios of the halides for plates, see p. 96, also apply in this case.

It is rather curious that in many cases halides other than those of ammonium and potassium are used, and a maker of this class of papers on being asked the reason, stated that the resultant color of the prints and contrasts were governed by these various chlorides. This is a statement that the author has not been able to verify, as from a series of experiments, using the exact equivalent weights of ammonium, potassium, sodium, strontium, lithium and magnesium, not the slightest difference in color or contrast was observed. Still, convention has prescribed the use of other halides, and the formulas are given as used commercially. From a theoretical point of view, one would assume that the lithium halides would be the most satisfactory salts to use, as they naturally give less nitrate than the others, but the nitrate is probably too hygroscopic and the prices too high.

CONTRAST PAPER.—

Potassium bromide	13	g
Strontium chloride, cryst	433	g
Gelatine	625	g
Sodium acetate	100	g
Alcohol	160	ccm
Hydrochloric acid	25	ccm
Water	5000	ccm

Temperature 50° C. (122° F.). Add:

Silver nitrate	500	g
Water	1650	ccm

Digest one hour at 60° C. (140° F.), and add:

Chrome alum	3	g
Hydrochloric acid	25	ccm
Cupric chloride	5	g
Water to	11000	g

The control of the contrast is determined by the quantity of the acid and copper solution; reduction of these reduces the contrasts.

SOFT-WORKING PAPER.—

Potassium bromide	25	g
Sodium chloride	200	g
Citric acid	50	g
Gelatine	625	g
Alcohol	250	ccm
Water	5000	ccm

Temperature 50° C. (122° F.). Add:

Silver nitrate	500	g
Water	1660	ccm

Digest at the above temperature for seventy-five minutes and add:

Chrome alum	3	g
Water to	11000	g

It will be noted that both these formulas contain a fairly high ratio of gelatine in mixing, and are then diluted down to the required bulk. This is to prevent the formation of a coarse grain. With all paper emulsions saponin or the quillaia tincture should be added, see p. 152.

STRIPPING PAPERS.—It may possibly be useful to indicate how a stripping paper may be made, that is to say, one with which the finished picture may be stripped from its support and transferred to another.

This is made by giving the paper a preliminary coating that is soluble in warm water. It will be found that baryta paper gives the best results, and it should be coated with one of the following mixtures:

A.	Soft gelatine	75	g
	White sugar	50	g
	Glycerine	25	ccm
	Water	1000	ccm

Or:

B.	Soft gelatine	150	g
	Starch	37.5	g
	Water	1000	ccm

In both cases the gelatine should be soaked in the water for thirty minutes, then melted, the other ingredients added and filtered. In the case of the second solution, the starch should be rubbed up into a cream with about a fifth of the water and boiled till a clear paste is formed, and then added to the gelatine solution. Both these may be coated in the usual way, but a thin film being required. It may be noted that in the use of stripping papers it is advisable to warn users against the employment of hardening baths, or the picture may not strip.

PRINTING-OUT EMULSIONS. — In this type of emulsion there is always some silver chloride and an organic salt of silver, usually the citrate or tartrate, free acid and an excess of silver nitrate, and they are also unwashed emulsions.

The action of light on silver chloride is to set free chlorine with the formation of silver subchloride. The reaction would be reversible and the free chlorine would attack the subchloride, to form colorless silver chloride again, were it not for the presence of the free silver nitrate. This is instantly attacked by the chlorine with the formation of silver chloride and nitric acid. The acid would tend to attack the silver subchloride, but it finds an easier victim in the organic salt, which it converts into nitrate, setting free the organic acid.

The addition of the organic silver salts, therefore, not only increases the speed of the emulsion, but also the intensity of the image. Besides that, the organic salts are markedly more sensitive to the less refrangible rays of the spectrum than the chloride, and this naturally makes the paper more sensitive.

The organic salts give greater contrasts in the prints.

The preparation of a printing-out emulsion is a comparatively easy matter, and the results, with constant conditions of working, very uniform. In all cases such emulsions should be made by yellow light, as they are comparatively sensitive to white light, even artificial, though the action is not apparent at first.

Innumerable formulas have been given, but the following which have been proved commercially may be relied on. The first formula is that given by Valenta, and the paper keeps well, gives vigorous prints and tones well both in the combined and separate baths:

Gelatine	300 g
Ammonium chloride	8.75 g
Water	2180 ccm

Allow the gelatine to soak in the water for about thirty minutes, and then melt and add the chloride. Temperature 50° C. (122° F.). Then add:

Tartaric acid	8.75 g
Sodium bicarbonate	4.375 g
Alum	5.625 g
Water	440 ccm

Dissolve the acid in the water and add the soda. A fairly large vessel should be used, as there is considerable effervescence. Finally add the alum. Temperature 50° C. (122° F.). Add:

Silver nitrate	100 g
Citric acid	25 g
Water	500 ccm

Temperature 50° C. (122° F.). The emulsion can be coated at once after filtering, but a more rapid-printing paper is obtained by allowing it to stand at from 40° to 50° C. (104° to 122° F.) for from thirty to sixty minutes.

The above gives a glossy surface paper when coated on glossy baryta paper. A matt surface can be obtained by using a matt surface paper and reducing the quantity of gelatine to 250 g. The best medium to filter the emulsion through is glass wool, as this is less likely to cause trouble with the free silver than any other.

Another satisfactory formula was given by Beadle:

Gelatine	296 g
Alum	13.5 g
Rochelle salts	13.5 g
Ammonium chloride	9.6 g
Water	2350 ccm

Allow the gelatine to soak in the water for thirty minutes, then melt to 50° C. (122° F.) and add the salts. Then add the following at the same temperature:

Silver nitrate	100 g
Citric acid	54 g
Water	400 ccm

Digest and filter as advised above.

This also prints rapidly, keeps well and gives a long range of gradation. Greater contrasts can be obtained by adding small quantities of uranium, nickel or copper salts, but they are not so satisfactory as calcium chromate, which can be made as follows:

Chromic acid, cryst.	25 g
Water	100 ccm

Dissolve and add gradually with constant stirring enough pure calcium carbonate to make the solution permanently turbid. Then filter and wash the filter with sufficient water to make the filtrate measure 250 ccm. The addition of from one to five parts of this solution to every 1000 of emulsion shortens the scale of gradation. This must be used with caution, as its action is very marked.

In mixing these emulsions, it is advisable to run the silver solution into the salted gelatine in a fine stream, so as to avoid a coarse grain. An alternative method, which, however, in the writer's experience, offers no particular advantage, is to coarsely powder the silver nitrate and add dry to the salted gelatine with vigorous stirring.

An alternative plan for making the matt surface papers is to add some matting material to the emulsion, for instance kieselguhr (infusorial earth), as used by Lumière, or starch, recommended by Prestwich. The ratio of these additions is dependent entirely on the surface desired and this may vary from one to two per cent calculated on the total bulk of the emulsion. The method of incorporating the starch is given under matt emulsions, see page 157. The addition of 0.4 per cent of powdered resin dissolved in alcohol or ammoniacal alcohol has also been suggested, but this has not given such satisfactory results in the author's hands as starch.

It is frequently recommended to use ammonium citrate, instead of the fixed alkaline citrates or tartrates, and theoretically the effect should be approximately the same, but although repeatedly tried, the paper thus prepared possessed very poor keeping qualities.

COLLODION EMULSION. — Except for photomechanical work, the use of collodion emulsion has completely died out, and even in this field it is gradually being ousted by the gelatine process plate. For this reason the information has been limited to actually proved formulas, to the exclusion of a vast amount of matter.

For negative work, von Hübl's method of manufacture will be found quite satisfactory. Either a pure bromide or a bromo-chloride emulsion may be used, and the latter is more suitable for color work.

Before proceeding to the actual formation of the emulsion, it is necessary to deal briefly with the pyroxylin and raw collodion. As a rule a high-temperature pyroxylin gives the best results, but as this differs with every maker, the specially purified kinds, sold under the names of celloidin, necol, pyralin, etc., should for preference be adopted.

Naturally, the viscosity of the resultant collodions differs with almost every sample of cotton. A thin fluid collodion is unsuitable, as it will not carry the silver halides, while on the other hand a more viscous sample is more difficult to work. It must be understood that viscosity is not entirely dependent on the ratio of pyroxylin to solvents, but on the physical properties of the same. It is well, therefore, to work with a collodion of given viscosity. There are various commercial viscosimeters, but they are all expensive, and some are not suitable because of the rapid volatilization of the solvents. The following simple method is quick and reliable. Take a glass tube fifteen centimeters long of two centimeters internal diameter, and draw out one end to a point, in which should be an aperture of one millimeter. The exact dimensions are not, of course, material, as long as they are approximated. At a convenient distance, about one centimeter from the wide end, make a diamond scratch on the outside of the tube. The viscosity is then obtained by the ratio of the time taken for the collodion to flow out compared to that taken by distilled water, or:

Collodion time ÷ water time = viscosity.

It is needless to point out that both the collodion and the water should be at a constant temperature, between 16° and 20° C. (60° and 68° F.), as the variations within these limits are negligible. The tube should be filled with water up to the diamond mark, and with a stop-watch the time taken for the tube to empty should be noted, and a mean of six runs should be taken. The tube should be thoroughly dried and the run of the collodion taken in the same way. For those who do not want to take the trouble to make such a tube, an ordinary fifty cubic centimeter pipette may be used, if the lower end is cut off within about half an inch of the bulb. The viscosity for a collodion should be from 1.57 to 1.60.

A pure bromide emulsion may be made as follows:

Pyroxylin	18 g
Alcohol	225 ccm

Shake with a rotary motion till the cotton is thoroughly wet and add:

Ether	225 ccm

Shake till dissolved. Make the following solution:

Silver nitrate	40 g
Water	50 ccm

Dissolve and add:

Ammonia	q. s.

to give a clear solution. Then add:

Alcohol, absolute	100 ccm

Allow the solution to get quite cold, 18° C. (65° F.), before adding to the collodion. This should be added in three or four lots, shaking well after each addition. Allow to stand for a minute or two and then add in the same way:

Ammonium bromide	30 g
Water	35 ccm
Absolute alcohol	70 ccm

Heat gently till dissolved. Allow the emulsion to stand five minutes. Then add distilled water in 5 ccm lots, shaking after each addition, till the emulsion separates out into fine flocks. Then pour into ten times its volume of water, the latter being well stirred all the time with a circular motion.

This is a little troublesome and time-consuming, but it precipitates the emulsion in fine flocks that are very easy to wash. The flocks should be allowed to settle, the supernatant water poured off and the vessel again filled with water, well shaken and again allowed to stand for the flocks to settle, and this operation should be repeated four times in all. The emulsion should then be collected on a clean well-washed cloth, the ends of the latter gathered together so as to form a bag, and then swung round vigorously at arm's length to sling out as much water as possible. The emulsion should then be placed in a flask or beaker and enough alcohol added to just cover it, the whole stirred well for a few minutes, and the alcohol poured off. The emulsion should then be well drained and fresh alcohol applied, and again poured off. These operations are repeated three times, and the last time the flocks should be placed in a clean cloth and screwed round so as to express as much alcohol as possible.

The damp flocks should then be placed in a two liter flask and covered with 250 ccm of absolute alcohol, well shaken and allowed to stand twenty-four hours. Then 150 ccm of the alcohol should be poured off and 150 ccm absolute alcohol added, in which has been dissolved 0.5 g of narcotin. Finally 250 ccm of ether should be added and the whole allowed to stand for twenty-four hours, with an occasional shake during the first four hours. It should then be filtered through glass wool, or it may be filtered after the final addition of:

Alcohol	250 ccm
Ether	250 ccm

After thorough shaking, the emulsion is fit for use.

A still better formula was given by von Hübl, although it is more trouble to make, as zinc bromide is used and this should be tested for the actual bromide content, as the commercial salt frequently contains basic salts. On the other hand, if the pure salt be purchased and at once made up into a stock solution with alcohol, about twenty-five per cent, the titration may be avoided.

To titrate the bromide, 5 ccm of the twenty-five per cent solution should be added to 200 ccm of distilled water, and a few drops of ten per cent solution of potassium chromate added. An accurate five per cent solution of silver nitrate should also be prepared and placed in a graduated burette.

Into the dilute bromide solution some of the silver solution should be dropped, shaking the flask after each addition, till the red color caused by the formation of the silver chromate no longer disappears on shaking, and the whole solution appears a faint pink. The quantity of the silver solution run out of the burette should then be read off and the strength of the bromide calculated as follows: suppose 44 ccm of the silver solution to have been used, then 5 ccm of the zinc bromide required 2.2 g of silver nitrate, therefore to convert 1 g silver nitrate, $5 \div 2.2 = 2.27$ g of zinc bromide are required. A twenty-five per cent solution of zinc chloride in alcohol should be made and tested in the same way.

To make the emulsion:

Pyroxylin	20 g
Alcohol	250 ccm
Ether	250 ccm

Dissolve as advised above and add:

Silver nitrate	50 g
Water	50 ccm

Dissolve by heat and add:

Alcohol	100 ccm
Nitric acid	0.5 ccm

Shake thoroughly till any cotton thrown down is redissolved, and add enough zinc bromide to convert 42 g of the silver nitrate, which will be about 95 ccm. Then add 3 ccm of aqua regia, which can be made by gently heating equal volumes of hydrochloric and nitric acids.

By this process the silver bromide is usually thrown down in coarse flocks, but on standing with an occasional shake, a fine emulsion is formed. It should be tested to see that there is excess of silver nitrate, and allowed to stand till a drop or two on a sheet of glass appears greyish-violet by transmitted light, which will generally be in from twenty-four to thirty-six hours. Then the excess of silver must be converted into chloride by the addition of zinc chloride solution mixed with an equal volume of four per cent collodion, and finally excess of chloride should be tested by the chromate test. The emulsion is precipitated and washed as described above, and the flocks dissolved to make one liter.

A simpler method was also suggested by von Hübl, by which practically a pure bromide emulsion is formed. In this the silver collodion is prepared as described above and mixed with the following solution:

Ammonium bromide	27	g
Water	40	ccm
Alcohol	100	ccm
Lithium chloride, sat. alc. sol.	15	ccm

After mixing it should be allowed to stand, precipitated and washed as described above, and made up to a liter.

For orthochromatizing these emulsions the isocyanin dyes should be used. For green use 20 ccm of sensitol green (1 : 1000 alcoholic solution) per liter, or the same quantity and the same strength of the new dye pinaflavol. For panchromatizing, sensitol violet should be used in the same strength.

For lantern slide making, the use of collodion emulsion has completely died out, but to complete the information the following formulas are given:

Zinc bromide	30.5 g
Pyroxylin	26 g
Alcohol	500 ccm
Ether	500 ccm

Dissolve, and add in small lots:

Silver nitrate	26.5 g
Water	30 ccm
Alcohol	200 ccm

Then add a drop or two of nitric acid, and allow to stand twenty-four hours, then precipitate and wash as described above, and dissolve to one liter.

The following is an easily made chloride emulsion:

Zinc chloride	12.8 g
Alcohol	500 ccm

Dissolve, and add:

Pyroxylin	11 g
Ether	350 ccm

Dissolve, and add:

Silver nitrate	21.8 g
Water	11 ccm
Alcohol	150 ccm

Heat to boiling and add the chlorized collodion to this gradually with constant shaking. Allow to stand twenty-four hours to ripen. The plates should be well washed after the film has set. This gives any color from red to black, according to the exposure and developer.

Collodio-Chloride Paper Emulsions. — Attention should be paid to the viscosity of the collodion, see p. 111. Innumerable formulas have been given for these emulsions, and the following is typical and gives good results:

Pyroxylin	20 g
Alcohol	450 ccm

Shake till the cotton is thoroughly wet, and add:

Ether	500 ccm

When dissolved, add:

Citric acid	1.7 g
Lithium chloride, cryst.	1.7 g
Strontium chloride, cryst.	3.4 g
Alcohol	20 ccm

Then add:

Silver nitrate	7.5 g
Water	20 ccm
Glycerine	2 ccm
Alcohol	30 ccm

Dissolve the silver in the water by the aid of heat, add the alcohol and glycerine and heat to 40° C.

(104° F.), and add gradually to the collodion. Allow to stand an hour to ripen, then coat.

SELF-TONING COLLODIO-CHLORIDE PAPERS. — The use of collodion as a vehicle for printing-out papers preceded that of gelatine, but at the present time its use is almost exclusively confined to the self-toning papers, which cannot be so satisfactorily prepared with gelatine in consequence of the coagulation of the gelatine by the gold salts used. Although this can be overcome, the paper has but poor keeping qualities.

The following formulas are given in order to complete the information, but with the exception of the first one, which was commercially prepared, they are taken from various patent specifications, but will at least serve as a basis for experiment. As regards the patent question, it is quite possible to validly patent a particular combination of salts, but the use of gold chloride in a print-out emulsion was clearly outlined by J. Spiller[1] in 1869.

Pyroxylin	125 g
Alcohol	2775 ccm
Ether	2775 ccm
Citric acid	100 g
Calcium chloride, anhydrous	7.75 g

Tease the cotton into a fluffy mass and pour the alcohol over it. When it is thoroughly wet, add the ether, the chloride and the acid, shake well, and add:

Silver nitrate	16.6 g
Ammonia	q. s.
Alcohol	160 ccm

Powder the silver and cautiously add the ammonia, almost drop by drop, till a perfectly clear liquid is obtained, then add the alcohol, and add to the chlorized collodion in small quantities with vigorous shaking. Then add the following:

Silver nitrate	83.4 g
Water	27 ccm
Glycerine	13.5 ccm
Alcohol	390 ccm

Finally add with constant shaking:

Gold chloride	2.5 g
Aluminum nitrate	4.5 g
Alcohol	75 ccm

This gives a glossy paper; for a matt surface, add to every liter 10 ccm of a ten per cent solution of white shellac in alcohol.

J. F. Kolby [2] patented an emulsion of

Lithium chloride	15.38 g
Or strontium chloride	23 g
Gold chloride	7.67 g
Silver nitrate	100 g
Collodion	3846 ccm

P. E. Schoenfelder & E. Kehle [3] patented the following:

Collodion, 3%	4816 ccm
Gold chloride, 6.25% alc. sol.	65.8 ccm

Then add:

Citric acid	21 g
Alcohol	21 ccm

Then add:

Silver nitrate	100 g
Alcohol	337 ccm

Add finally:

Strontium chloride	10.5 g
Alcohol	21 ccm
Glycerine	21 ccm

Iridium, rhodium, osmium, palladium or platinum salts might be used instead of the gold salt.

O. Raethel[4] patented:

Silver nitrate	100 g
Water	122 ccm
Alcohol	182 ccm

Dissolve, and add:

Collodion, 3%	2448 ccm

Then add:

Chloride	31 to 49 g
Water	122 ccm
Citric or tartaric acid	25 g
Alcohol	122 ccm

To this emulsion should be added:

Gold chloride	0.144 g
Ether	70 ccm
Alcohol	130 ccm
Barium chloride	1.44 g
Collodion, 3%	288 ccm

H. Luttke[5] patented the use of the nitrate of gold in place of the chloride, or the sulphate or a compound of the latter with lithium. In his first patent there was no free silver nitrate, but in the later ones only thirty to fifty per cent of the silver nitrate was converted, and this gave much more vigorous prints. His formula was:

Celloidin collodion, 4%	2480 ccm
Ether, 0.720	400 ccm
Alcohol, 96%	120 ccm

Add:

Silver nitrate	100 g
Water	100 ccm
Alcohol	480 ccm
Lithium-gold nitrate	5.6 g
Or aurous sulphate	3.6 g
Or lithium-gold sulphate	5.2 g

Then add:

Potassium chloride, anhydrous	12 g
Or lithium chloride, anhydrous	8 g
Citric acid	20 g
Alcohol	120 ccm

O. Steudel[6] contended that good tones could not be obtained with gold chloride alone, and patented the use of from ten to sixteen parts of lead nitrate and 2.5 parts of gold chloride to 100 parts of silver nitrate. The addition of lead salts certainly facilitates the obtaining of brown tones; but possibly the action is due more to the combination of the lead salt with the hypo in the fixing bath than any other specific action. M. Baur[7] patented the use of fulminating gold, that is gold chloride with the addition of ammonia.

C. S. Poulsen[8] varied the process by the use of a dye and an alkaline cyanide or sulphocyanide, thus 0.005 to 0.015 g of methyl violet or fuchsin with 3 to 6 g of cyanide or sulphocyanide and 2 to 3 g of gold chloride were to be added to every liter of emulsion. The patentee claimed that the dye prevented reaction between the silver nitrate and the gold salt, and therefore the paper kept better.

SILVER PHOSPHATE EMULSIONS. — The use of this salt has been much neglected, as it will give the nearest approach to a black print that it is possible to obtain by printing out. There are two reasons for failure, one the extreme sensitiveness, the other the very long range of sensitiveness, which results in very flat prints. As a matter of fact the sensitiveness is so great that the emulsion cannot be prepared with safety except in an orange light, and the range of gradation is so great that even with a contrasty hard negative the highlights show a marked tinge before the shadows have attained their full density, and by the time the latter are deep enough the former are deeply tinged. Both troubles are easily overcome, the first by using the proper light in the making and coating, and the second by the addition of a suitable contrast-increasing agent. With gelatine as the vehicle the color of the images is more of a brown than with collodion.

If the phosphate of silver is formed by the reaction between sodium phosphate and silver nitrate, the prints are wanting in depth, and one has the formation of free nitric acid, as shown by the following reaction:

$$Na_2HPO_4 \, . \, 12H_2O + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3 + 12H_2O$$

This free acid must be neutralized or the silver phosphate will be dissolved. One can use the sodium tribasic phosphate, thus:

$$Na_3PO_4 \, . \, 12H_2O + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3 + 12H_2O$$

Then there is no free acid. It is obvious that practically 75 parts of the tribasic phosphate are required to convert 100 of the nitrate, and that 134 of silver nitrate are required to convert 100 of the phosphate and that the quantity of silver phosphate produced is 110 for every 100 parts of the sodium phosphate.

Unfortunately the tribasic phosphate is insoluble in alcohol and ether, but there is no reason why it should not be dissolved in a small quantity of water and added to the silver collodion, as is frequently done with insoluble salts in the collodiochloride process.

As regards the long range of sensitiveness and consequent flatness of the prints, one can easily use calcium chromate or small additions of uranyl, copper or nickel chlorides, as suggested by Valenta for the hardening of the contrasts in the chloride emulsions.

The use of silver phosphate as the sensitive salt in printing-out dates back to the very earliest days of photography in 1839, by Fyfe, who dissolved it in ammonia or ammonium carbonate and impregnated plain paper therewith. Valenta[9] paid considerable attention to this salt and recommended the following method of making the emulsion with phosphoric acid:

Collodion, 4%	2087 ccm
Ether	314 to 417 ccm

Add:

Phosphoric acid, sp. gr. 1.265	28.5 to 29.3 ccm

Then add:

Citric acid	68.5 to 80 g
Alcohol	137 ccm

Add:

Silver nitrate	100 g
Hot water	115 ccm
Alcohol	206 ccm

Shake thoroughly, and add:

Lithium carbonate	5 to 10 g

Add till there is no longer evolution of carbonic acid. Then add:

Glycerine	15 ccm
Alcohol	15 ccm

It should be noted that it is far better to dilute the phosphoric acid with some alcohol, otherwise it becomes coated with a skin of precipitated pyroxylin and is very difficult to dissolve again.

This paper is three times as sensitive as the commercial collodio-chloride papers. It can be toned in the ordinary way, or if immersed in a two and one-half per cent solution of citric or tartaric acid till the yellow color disappears, it can be fixed after washing in a five per cent solution of hypo and gives a deep brown tone. The paper must be manipulated in an orange light. To ascertain the properties of this paper, an exactly similar emulsion was prepared, only replacing the phosphoric acid by equivalent quantities of strontium and lithium chlorides in the ratio of 2 : 1. Under a scale print-meter the phosphate emulsion showed four or five times greater sensitiveness than the chloride, and the range of gradation of the former was as 25 : 13. Freshly albumenized paper showed a lower degree of sensitiveness than the chloride, and a range of gradation of 18 degrees.

Comparative tests were made of mixtures of the phosphate with the chloro-citrate. Calling the former A and the latter B the following mixtures were made:

1. A 10 parts, mixed with B 90 parts
2. A 20 " " " B 80 "
3. A 30 " " " B 70 "
4. A 50 " " " B 50 "

Papers coated with these gave the following results:

No.	*Sensitiveness compared to chloro-citrate*	*Range of gradation*
1	2.5	17
2	3.8	18
3	4.1	20
4	4.7	over 20

These experiments show that by the addition of the phosphate it is very easy to increase the sensitiveness and range of a chloride emulsion.

Later Valenta pointed out that the addition of a chromate to a phosphate emulsion shortened the scale and thus made it more suitable for ordinary work, and suggested the following modification of his formula:

Collodion, 3 to 3½%	2174 ccm

Add:

Phosphoric acid	28.7 ccm
Citric acid	70 g
Alcohol	143 ccm

Then add:

Silver nitrate	100 g
Ammonia	q. s.

Powder the silver and cautiously add enough ammonia to form a clear solution, and add to it:

Warm alcohol	355 ccm

Add this silver solution to the collodion, shaking well after each addition, and finally add:

Ether	355 ccm
Glycerine	28.7 ccm

The instructions for making calcium chromate for giving increased contrast will be found on p. 109.

W. J. Wilson[10] patented the addition of sodium tungstate or molybdate to phosphate emulsions to increase contrasts. His formula was:

A.	Gelatine	400 g
	Water	4000 ccm
B.	Sodium phosphate	116.6 g
	Citric acid	100 g
	Water	1000 ccm
C.	Silver nitrate	100 g
	Water	1000 ccm
D.	Sodium tungstate	46.6 g
	Water	500 ccm

B and C are added alternately in small quantities to the gelatine solution, and then finally D. This paper was to be only briefly exposed, and physically developed with:

Metol	7 g
Glacial acetic acid	28 ccm
Water	6000 ccm

Fix in a hypo bath with an addition of sodium metabisulphite. All these phosphate papers can be developed in the same way.

Printing-Out Silver Bromide Emulsions. — Valenta also suggested the use of silver bromide in lieu of chloride for printing-out emulsions, the sensitiveness being about three times as great as the chloride emulsions:

Collodion, 2½ to 3%	5000 ccm

Add:

Citric acid	100 g
Alcohol	400 ccm
Strontium bromide, anhydrous	16 g
Glycerine	8 ccm

Then add:

Silver nitrate	100 g
Water	q. s.
Alcohol	400 ccm

Dissolve the silver in as little hot water as possible and add the alcohol. Finally add:

Ether	800 ccm

The silver solution must be added to the bromized collodion by yellow light. Allow the emulsion to stand for a few minutes and filter through glass wool.

The prints on this paper can be toned in the usual separate and combined baths, and they lose but little in toning and fixing. There is no tendency to bronzing. The gradation is greater than with ordinary chloride emulsions and therefore the addition of a little calcium chromate may be advisable. The addition of from 4 to 6 g of calcium chloride, anhydrous, to the above emulsion, gives a brilliant and vigorous printing paper which is three times faster than the normal chloride. This paper tones well and does not lose in fixing. Greater contrast can be obtained by using uranium chloride, 2 to 3 g, instead of the calcium salt.

LIPPMANN EMULSIONS. — These, as is well known, are used for Lippmann's interference heliochromy. They are extremely easy to make, but great care must be taken not to allow them to ripen, otherwise the grain becomes too coarse.

Valenta[11] suggested the following method:

A.	Gelatine	10	g
	Water	300	g
	Silver nitrate	6	g
B.	Gelatine	20	g
	Potassium bromide	5	g
	Water	300	ccm

Dissolve the gelatines and add the salts, and cool the solution to 35° C. (95° F.), then add A to B. Pour the emulsion into a liter of alcohol and stir with a glass rod till the whole of the emulsion adheres to the rod. Cut up the emulsion as fine as possible and wash for a short time in running water. Collect the shreds and add enough water to make 600 ccm. Melt at as low a temperature as possible.

Later Valenta gave the following formulas for chloro-bromide emulsions, which gave very brilliant results, and stated that he could not decide which was preferable:

A.	Gelatine	40 g
	Water	800 ccm
B.	Silver nitrate	6 g
	Water	60 ccm
C.	Sodium chloride	1.4 g
	Potassium bromide	1.4 g
	Water	60 ccm

Heat A to 35° to 40° C. (95° to 104° F.) and divide into two equal parts. Add B to one and C to the other, and then mix. Or:

A.	Gelatine	10 g
	Water	300 ccm
	Silver nitrate	6 g
B.	Gelatine	20 g
	Potassium bromide	2.4 g
	Sodium chloride	1.5 g
	Water	300 ccm

Heat both to 35° C. (95° F.) and treat as above.

These emulsions are extremely slow, and ripening in the ordinary way means coarsening of the grain. Valenta tried the addition of 0.1 g of sodium sulphite to 300 ccm of the emulsion, and digested at 35° C. (95° F.) for five, fifteen, and thirty minutes. He found there was increase of speed without coarsening of the grain.

Cajal preferred to add 0.75 g silver nitrate to the bromized gelatine which contained 0.55 g of potassium bromide at about 55° C. (131° F.). He considered that if the emulsion was gently stirred during the mixing a slow emulsion resulted, but that if the mixing was effected in a bottle with vigorous agitation a more rapid result was obtained. It was stated that the speed might thus be varied as 1 : 3. Instead of washing the emulsion, the plates were coated and washed after they had set, a plan originally suggested by Lippmann.

J. Gaedicke[12] used the exact equivalents of bromide and silver nitrate, a small addition of chloride being made to obviate any possible trouble from errors in weighing:

A.	Hard gelatine	20 g
	Potassium bromide	14 g
	Hydrochloric acid	0.4 ccm
	Water	400 ccm
B.	Gelatine	20 g
	Water	280 ccm
C.	Silver nitrate	20 g
	Water	120 ccm

Soak the gelatines in the water, add the salts to A (11.5 g ammonium bromide may be used instead of the potash salt), melt and cool to 37° C. (99° F.). Add C to B and then this to A, shake well and allow to set for twenty-four hours; shred through canvas under water, and wash for an hour in running water. Melt to 40° C. (104° F.), add gelatine, 60 g, which has been previously swollen and melted. Finally add 200 ccm alcohol, and make the bulk up to 2000 ccm, then filter.

H. E. Ives[13] found that there was a noticeable increase in the purity of the colors when the total quantity of silver bromide was reduced. His formula was:

A.	Gelatine	1.25 g
	Water	31 ccm
B.	Gelatine	2.5 g
	Potassium bromide	0.3125 g
	Water	63 ccm
C.	Silver nitrate	0.375 g
	Water	6 ccm

A and B should be heated till the gelatine melts, allowed to cool to 40° C. (104° F.) and C added to A, then A and B slowly mixed with stirring. The sensitizing color is added, the emulsion filtered and the plates coated, washed for fifteen minutes when set, and dried. Previous to Ives' work it was always assumed that the plates had to be coated very thinly, but he proved that with a film thickness up to 0.1 mm, increased purity of the colors resulted, at least in spectrographic work.

The earlier color sensitizers used were cyanin, alone or mixed with glycin red, etc. But better results are obtainable with some of the newer isocyanins, particular isocol (Ives) or sensitol violet, 1 ccm of a 1 : 1000 alcoholic solution to 100 ccm emulsion.

R. E. Liesegang[14] suggested a method of making Lippmann plates, a modification of earlier ones, which saves a good deal of trouble, and yet gives excellent results. Coat the glass with six per cent solution of gelatine containing three per cent of potassium bromide, and as soon as the film has set immerse in five per cent solution of silver nitrate. This gives a very fine grained plate, but the film must not be dried before immersion in the silver solution, and the latter must be kept well in excess. These plates must be physically developed with an acid developer, pyrogallol for preference.

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[1] *Phot. J.*, 1869; *Phot. News*, 1869, **13**, 401. Cf. E. J. Wall, *Brit. J. Phot.*, 1921, **68**, 198.

[2] *D. R. Pat.* 77,162, 1893

[3] *Eng. Pat.* 6,651; 15,852, 1896; *U. S. Pat.* 560,755; 560,756; 568,496, 1896.

[4] *D. R. Pat.* 110,089, 1897; *Eng. Pat.* 19,683, 1897.

[5] *D. R. Pat.* 132,421, 1899; 135,318, 1901; *Eng. Pat.* 17,950, 1901.

[6] *D. R. Pat.* 176,323, 1906; *Eng. Pat.* 10,051, 1906.

[7] *Eng. Pat.* 28,284, 1902.

[8] *Eng. Pat.* 19,850, 1905; *D. R. Pat.* 190,926, 1905.

[9] *Phot. Korr.* 1900, **37**, 313, 449; *Brit. J. Phot.* 1900, **47**, 325; *Phot. J.*, 1900, **40**, 149. Fyfe's note on the use of phosphate will be found in *Edin. Phil. J.*, 1839, 144. Maxwell Lyte, *Phot. J.*, 1856, **3**, 50, used phosphate for albumenized paper and later, *ibid.*, 253, with tartrate of soda, sugar of milk and gelatine. J. Meyer, *D. R. Pat.* 114,868, 1899, dissolved silver phosphate in an organic acid in conjunction with collodion or gelatine as the vehicle. York Schwartz, *U. S. Pat.* 710,019, 1903; *Fr. Pat.* 320,451, 1902, also patented the use of silver phosphate.

[10] *Eng. Pat.* 10,284, 1909; *Brit. J. Phot.*, 1910, **57**, 122.

[11] *Phot. Korr.*, 1892, **29**, 432.

[12] *Handbuch*, **3**, 26.

[13] *Astrophys. J.*, 1908, **27**, 323.

[14] *Phot. Rund.*, 1915, **51**, 198.

For general reference, consult "Die photographischen Kopierverfahren mit Silbersalzen" by Fritz Wenzel (1928), which is Vol. IV, Part I of Eder's "Ausführliches Handbuch der Photographie."

CHAPTER VII

MIXING DIFFERENT EMULSIONS

IT naturally occurs to one that, given a fast emulsion with low gamma infinity and a comparatively slow one with a high gamma, a mixture of the two should combine the virtues of both. One may put the matter a little more precisely: suppose one has an emulsion of 250 H. & D., with a gamma infinity of 1.3, and a slower emulsion of 25 H. & D., with a gamma of 3, will a mixture of the two in equal volumes give a speed of 137 and a gamma of 2.15? The answer is in the negative; at least, that is the writer's experience. That there is an improvement by the admixture of the slower emulsion cannot be denied, but the result is not the mean. Eder[1] says: "If a very sensitive but not quite clean-working emulsion is mixed with an unripened emulsion, the result is very satisfactory, as first stated by the author (Eder) in 1882.[2] Even one-tenth to one-twentieth of the latter produces perfect cleanness as well as less vigor, and does not markedly detract from the sensitiveness. On the contrary more details are brought out by longer development. The addition of too much unripened emulsion lowers the sensitiveness. By this and similar skilled mixtures the density of an emulsion may be considerably increased without the sensitiveness suffering." This statement as to the reduction of fog has not been borne out in practice, to such an extent at least as to be of any commercial value. If large quantities of the clean-working emulsion are added, one would naturally have less fog because there are fewer foggy grains per unit area.

W. K. Burton[3] dealt with this subject and concluded that in mixing emulsions of no very great differences of sensitivity — say not more than four to one — first, the particles of the more sensitive emulsion require a greater amount of light to produce a developable reduction than before the mixture. Secondly, particles of the slower emulsion, which, with the emulsion used alone, would not be reduced at all, are reduced in the presence of the more rapid emulsion. Thus it appears that, by mixing equal parts of two emulsions whose sensitiveness does not differ greatly, we get an emulsion more rapid than the mean of the two, and giving about as great density of the highlights and also details, as would be got with the more rapid emulsion alone. But he is careful to point out that when the speeds differ greatly, the slower emulsion merely acts as so much inert matter and is not reduced at all. Were it possible to mix not only the emulsions as such, but also the silver grains, one would undoubtedly obtain totally different results, but when the grains are totally distinct there may not be transference of the chemical action from the one grain to the next.

It should be pointed out that in the early days the methods of testing emulsions were by no means so precise as at the present time and therefore, statements of those times must be accepted with some reserve.

The mixing of batches of the same formula and method of making can, however, be utilized to obtain wonderful regularity of results. Let us assume that half a dozen batches are made on each of three successive days and these are all mixed and half coated as a commercial batch, and the other half mixed with another set of like emulsions, and half again coated. It is obvious that the first and last batches will probably be more alike than if each batch is coated separately. In this sense the mixing of emulsions is extremely valuable.

[1] *Handbuch* **3**, 204.
[2] *Phot. Korr.* 1882, **29**, 149.
[3] *Brit. J. Phot.* 1884, **29**, 278.

CHAPTER VIII

SHREDDING AND WASHING THE EMULSION

THE emulsions as prepared contain excess of soluble bromide and alkaline nitrates, which if not removed would crystallize out on the plates, during drying. As these salts are held in solution in the jelly they must be removed by diffusion, and the greater the surface presented to the water the more rapid the diffusion. As the jelly is set in a pot or poured out into a dish, it is obvious that in such form the diffusion must be very slow and if in thick lumps would probably not be complete in any reasonable time. It is customary, therefore, to break up or "shred" the emulsion, and the method adopted will naturally differ according to the total bulk, that is to say, whether for amateur or commercial work.

Assuming that a small batch only has been made, and this has been poured out into a flat dish to set, one of the simplest plans is to score the emulsion across with a silver fork so as to break it up into narrow strips. It should be noted that emphasis is laid on the silver, and this is preferable to plated or other metal forks, thus avoiding possible contamination and desensitizing, which may happen, particularly with ammoniacal emulsions. It is not well to score across the jelly in two directions, as this breaks it into too small pieces, which pick up too much water during washing. If it is set in bulk in a jar, the best method is to use coarse canvas with not less than quarter inch mesh.

A good sized piece should be used, which should be preferably boiled in five per cent solution of carbonate of soda for about five minutes to remove grease and dressing, then thoroughly washed in cold water to remove the soda. To use this, spread it out flat and place the jelly, broken up into small pieces about the size of a walnut, in the middle, then gather the ends of the canvas together so as to make a bag and, holding these in the left hand, immerse the bag in cold water and with the right hand twist the ends, when the jelly will be forced through the meshes. The idea of doing this under water is to keep the worms separate and prevent the heat of the hands from melting them. " Shreds," " worms " or " noodles " are all shop terms for the broken up jelly. When all the emulsion has been squeezed through, the canvas may be washed thoroughly in hot water, after first rinsing in cold, and dried, and may be used again and again.

It is also possible to use one of the small sausage machines for this work. These can be obtained, made of tinned iron and with various face plates through which the material is forced. The plate with largest apertures should be used. It has been recommended to coat these machines with shellac varnish; but this is not advisable, as the varnish nearly always flakes off, particularly with ammoniacal emulsions. It would at first sight seem that there is great danger of contamination of the emulsion from the metal of these machines, but this has not been met with, provided it is kept clean and free from rust. After use the machine should be disassembled and all parts well washed in boiling water, till there is not the slightest sign of milkiness and then if removed from really hot water, they will dry quickly with absolute assurance of no rust.

For commercial work power presses will naturally be used. The usual form is a cylinder, preferably phosphor bronze, about twenty-seven inches long and of six inch bore, with a piston travel of twenty-four inches. The face of the piston should be hard rubber and the inside of the cylinder must be silvered, preferably with not less than a six ounce deposit. But even this can be improved by the use of a solid silver lining, which can be easily sweated in. Plating nearly always wears off in time and lays bare the underlying metal. The bottom of the cylinder carries a solid silver plate, through which the jelly is forced. The perforations are preferably circular, of about three-eighths inch diameter and with one-sixteenth inch clearance between the circles. There is naturally some difference of opinion as to the size of the holes, but the above has been found to work well in practice.

Hydraulic power will be found the most satisfactory, as screw presses are slow and exhausting to work. The water pressure should not be less than twenty pounds per square inch, in fact this may be said to be the minimum allowable, for one wants a reserve in hand for extra stiff jellies. As a rule, a constant pressure will be sufficient, though some people prefer to work slowly, and then a variable regulating valve should be placed in the supply pipe. The cylinder should be mounted on a wooden frame, cypress for preference, and the frame should be of such a height that the operator in filling the cylinder with emulsion may have as little handling as possible. The frame should be of four by four inch posts, firmly bolted to the floor, and on one side should be arranged a table, at such a height as will just allow the top of the crock to be level with the top of the cylinder, so that the workmen can readily drop the blocks of jelly into the cylinder. Underneath the cylinder, between the posts, should be a shelf at such a height as will allow a crock to be placed, so that it can receive the worms. No actual measurements can be given, as these will depend on the size of the crocks used.

The receiving crock should have a capacity at least double that of the mixing pot, and should be about half filled with cold water, so as to keep the worms separate. In one establishment the crock was raised sufficiently high and filled with enough water so that the end of the cylinder was always below the surface of the water. It is probably needless to point out that the press should be located in the washing room, so that there will be no need to carry the crock any distance.

As regards the washing of the emulsion, opinions differ widely and each manufacturer has his own pet scheme. Dealing first with the amateur emulsion maker's problem, this will depend to a great extent on the quantity of emulsion made; but assuming this to be approximately a liter, there is no better way of washing than merely tying the worms up in a square of coarse linen, gathering the ends up into a bag, and suspending in a vessel of water by means of a stick laid across the mouth of the jar. The bag should be suspended so that it is completely immersed in water, and should be at least three inches from the bottom of the vessel. The salts thus diffuse into the water, and if the bag be gently pressed between the hands every five minutes or so, while it is still in the water, the action will be better. The water can be changed every five or ten minutes, and the bag gently twisted so as to express as much water as possible. If this operation be repeated every five minutes for an hour, the emulsion may be considered to be properly washed.

This naturally entails some little expenditure of time and trouble and, to avoid this, one may adopt the following method which is very efficient. Procure a large jar *A,* as shown in Fig. 5, into the mouth of which is fitted a good bung, through which should be bored two holes, one at the side, *C,* taking a short piece of glass tubing, and the other one in the center of the bung large enough to take the stem of an inverted funnel, *B,* which must be small enough to pass through the mouth of the jar. One end of *C* is connected with the water tap *E* by a piece of rubber hose *D,* while to the other end is also fastened a rubber tube, *F,* long enough to reach to the bottom of the jar. To the end of the stem of the funnel is also attached another rubber pipe *G,* which acts as a waste pipe. The mouth of the funnel may be covered with muslin, which can be easily held in position with string or a rubber band. The worms are placed in the jar, and the water turned on with sufficient force to keep them constantly on the move. If a stoneware jar be used, there is less likelihood of any possible light action. With a sufficiently large jar, one holding about two gallons, and a good supply of water, it is possible to wash a couple of liters of emulsion in this way in an hour.

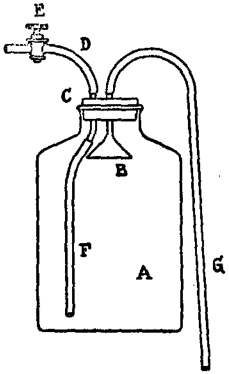

FIG. 5

There is one point to which attention should be drawn, and that is that every tap through which water is drawn for washing emulsion should be fitted with a filter. These can be obtained at very little cost and are so arranged that the filtering medium, usually absorbent cotton pads, can be frequently changed. There are few water supplies that are free from impurities, and there is always great danger of the water picking up rust from the pipes. In one case in the writer's experience a pad of absorbent cotton half an inch thick became so choked with dirt in half an hour that but a mere dribble of water could force its way through, and the cotton when removed was deep reddish black from rust and dirt.

The washing water should be as cold as possible, and if possible its temperature should not exceed 15° C. (59° F.) while 10° to 12° C. is better. The warmer the water, the more rapid the diffusion of the salts, but the more water the worms pick up, and this may cause great trouble in hot weather. For commercial work, in some cases, large tanks are provided, through which the pipes of a brine or ammonia refrigerating system are led to reduce the temperature of the water. Probably the most economical system is one in which a coil of water pipe is fitted with an internal cooling pipe. While a little elaborate and costly to install in the first place, the most efficient system was installed by the writer on these lines. The whole system was built on the walls of the washing room, and was thus quite out of the way, and took up no valuable room. It consisted of six rows of three inch cast iron pipe, all connected at both ends with elbows. Through the center of each pipe ran an ammonia pipe, all being led off one main, and each provided with a valve so that the ammonia could be shut off, if required, from any number of sections. With this arrangement, the washing water, which in the height of summer entered the pipe at a temperature of 24° C. (75° F.), was delivered to the washing tanks at 15° C. (59° F.).

Of the many methods used for washing in commercial establishments, there are some which are more efficient than others. The various designs seem to be based on ideas peculiar to each maker, and this rests on the question of rapid or slow washing. That the duration of washing can exert considerable action on the emulsion is an accepted fact, and one may encounter the so-called " washing fog," which is generally the result of long washing or too high a temperature of the water. On the other hand, it is possible for an increase in speed to take place without increase of fog, and this is sometimes reckoned on by the emulsion maker as an essential part of the process, but unless the temperature of the water is kept under complete control, it is a somewhat dangerous and variable factor, that should be eliminated as far as possible.

The duration of washing depends on the quantity and hardness of the jelly; but in normal factory practice this can generally be relied on as being fairly constant. In the early days, or even as late as 1892, from twelve to eighteen hours' washing was not uncommon, but of recent years this time has been much curtailed, in some cases to four to six hours and in others even to half these latter times.

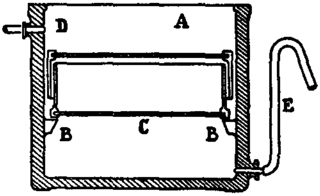

Fig. 6

One of the oldest methods, and in the writer's opinion the least efficient, is the double sieve method, as in Fig. 6, in which *A* is a stoneware vessel with projecting ears *BB*, about one-third of the way from the bottom inside. On these rests a fine hair sieve *C,* the frame of which is constructed entirely of wood. The worms are placed in this sieve and another sieve over the top. At *D* is the supply pipe and *E* is a siphon waste pipe. With this arrangement the worms have a great tendency to pack together and, unless in a very thin layer, the center shreds do not get properly washed. A far better plan is to reverse the direction of the water, and make *E* the supply and *D* the waste pipe; there is then a better circulation of water through the emulsion, assuming that the sieve sits sufficiently tight on the ears to allow no water to pass, though even with this the water naturally takes the path of least resistance.

A German type of washer is shown in Fig. 7. The emulsion is placed in a cloth bag and hung in an upright cylinder, the water flowing into the top and out at the bottom. The objections to this are the compacting of the shreds, as in the double sieve arrangement. As an improvement on this a wooden rod has been passed down the center of the bag and tied to the bottom. The upper end of the rod is connected with an eccentric working on a shaft, so that the bag is alternately raised and lowered; the water runs in at the top continuously. In another arrangement flat-sided bags were about half filled with emulsion, then laid on

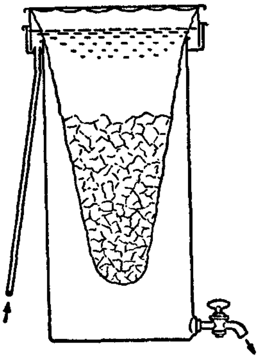

Fig. 7

their sides in a trough through which ran a stream of water, a flat board above each bag being alternately raised and lowered by an eccentric, so that the water was constantly pressed out of the bags.

The objection to all methods in which cloth, usually unbleached calico, is used is that the fibers of cloth soon become choked with earthy salts from the water, and then there is little circulation of water through the cloth. There is also always danger of a slipshod workman scamping the washing of the bags, for they must be well washed after each time of using, or after a day's run.

The most efficient systems are those in which the worms are kept in constant motion so as to be brought into continuous contact with ever-changing water. This may be effected by the water supply itself or mechanically. In Fig. 8 is shown one form of washer in section, in which *A* is a conical wooden tank into the bottom of which is led the water supply *E*. *B* is a wooden ring, covered with muslin, that springs under the exit pipe *D* and the lug *C;* the sole purpose of the muslin is to prevent the small worms from being washed down the water pipe. The cone is supported on trunnions and after washing, the entrance pipe, which must be flexible, is unscrewed, a crock placed under the machine and the emulsion allowed to run out.

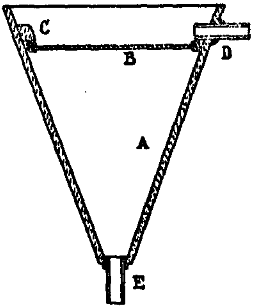

FIG. 8

In another arrangement, which can be built of cypress wood, a coil of block tin pipe is laid on the bottom and nearly covered with a fine cement, such as plaster of Paris, just leaving the top of the pipe exposed, through which are punched a series of holes through which the water enters. The center of the tub should be fitted with an overflow pipe so arranged that the level of the water is always within about three inches of the top of the tub, and this pipe should be provided with a muslin cover to prevent the shreds from washing away. The sides of the tub may be about eighteen inches high and the diameter be from two to three feet.

Another arrangement is nothing more than a barrel supported on an axle, which is hollow and through which the water is supplied. A small section is cut out of one side of the barrel for loading with emulsion. The axle is provided with a series of arms and cross paddles, but the body of the barrel is made to turn, so that the water and emulsion are being constantly churned up, and the water flows away at the end opposite to that at which it enters.

The most efficient washer that the writer has used was an enamelled, so-called glass-lined tank of nearly circular section, provided at the bottom with a wire grating, which was always covered with muslin. The water escaped through a siphon pipe at one side under the grating, and entered at the top. A rod in the middle of the tank supported by arms from the sides carried a couple of propeller blades which worked to within a couple of inches of the bottom. The tank was filled with water, the shreds dumped in and the propeller set in motion by an overhead motor, or grooved wheel and belt working on a countershaft. With such an arrangement the motion of the propeller blades, which can be made of bakelite or similar composition, creates a most efficient churning and there is not the slightest chance of inefficient washing. To empty such a tank, the water supply is cut off, the revolution of the blades stopped and the water allowed to run out. It is then easy to collect the emulsion.

It is, of course, necessary to determine when an emulsion has been properly washed. Some firms make a practice of doing this with each batch, others merely at intervals to check up. Assuming that one has to deal with the elimination of bromides, probably Volhard's sulphocyanide test is as satisfactory as any.

CHAPTER IX

PREPARING THE EMULSION FOR COATING

WE have so far practically left the emulsion in the washing room and we can now follow it on to its final resting place in the stock room.

There is a good deal of water adherent to the washed worms, and as a rule they are merely left to drain for an hour or so. This, if the worms are spread out, is more or less effective. Some manufacturers rinse them with distilled water so as to remove to some extent the adherent water containing lime salts, etc., then allow to drain. The only variation on this draining process that the writer has seen was adopted by one maker, who spread the emulsion out in a thin layer on long cloth trays and passed a strong current of dry air through it for two hours. This is a rather unnecessary refinement, because water must almost invariably be added to make the bulk up to a given volume, as, if the washing water is cold, the worms will not have picked up enough.

If the emulsion is not to be used at once, the worms should be melted at as low a temperature as possible, not more than 40 C. (104 F.), and kept at this temperature for an hour or so, to allow the occluded air to rise. The emulsion should then be thoroughly set in the ice room, and alcohol, containing 0.5 per cent of pure phenol, poured on the top to the depth of about one half to three quarters of an inch. This seals the surface and prevents to some extent the growth of bacteria. When the emulsion is required for use this alcohol can be poured off and the emulsion melted in the usual way. Homolka[1] kept rapid emulsions in this way for a month. When required for use, the benzol is poured away and the last remains of it allowed to evaporate.

The usual additions to an emulsion are: some hard gelatine, the quantity varying according to the method of coating and the character of the emulsion; some alcohol; an antiseptic, such as thymol or phenol; "blue doctor" for plates; and for paper work some "brown doctor."

The quantity of alcohol naturally varies, but about eight per cent is usual. The quantity of antiseptic is generally about one per cent. Blue doctor is the shop term for chrome alum solution, basic chrome alum being usually employed. This can be made as follows:

Chrome alum	100 g
Water	500 g
Ammonia	q. s.

Dissolve the alum by heat and add sufficient ammonia solution to form a slight permanent precipitate after thoroughly stirring, then filter and add:

Glacial acetic acid	20 ccm
Water to	1000 ccm

Another method (Cobenzl) is to proceed as above as far as the formation of the precipitate and then boil the solution and add more ammonia till a permanent precipitate is formed, then filter and wash the filter to make 1000 ccm in all, the acetic acid being omitted.

The purpose of the chrome alum is to harden the gelatine and prevent frilling. Consequently the quantity used depends on the total quantity of the gelatine and not on the bulk of the emulsion. Naturally the ratio varies with each maker and this ranges from one of chrome alum, or ten parts of the above basic solution, to two hundred and fifty or three hundred parts of dry gelatine. It will be seen from p. 99 that Wratten used tannin for the same purpose.

Under no circumstances should formaldehyde be used as a hardener. This inevitably, according to the writer's experience, leads eventually to fog on keeping.

Brown doctor is the shop term for a semi-alcoholic tincture of quillaia bark, *Quillaia saponaria,* and different formulas have been given for this. The first is one largely used in England:

Quillaia bark	250 g
Alcohol	250 ccm
Water	750 ccm

Macerate for sixteen days and then filter. Cobenzl recommends:

Quillaia bark	1000	g
Alcohol	1000	ccm
Water	1000	ccm

Digest for two days in a warm place and filter. The bark should be coarsely powdered, so as to pass a sixteenth-mesh sieve.

The quantity used varies according to the ideas of the maker and it is frequently omitted altogether from plate emulsions, being confined solely to paper and film emulsions. Of the first solution above seventy-five parts should be added to one thousand parts of emulsion, of the second one to one thousand. Another formula is:

Quillaia bark	100	g
Alcohol	1000	ccm

Digest for forty-eight hours and filter; of this, one hundred and twenty-five parts to a thousand were used. Instead of using the bark, some manufacturers use saponin itself, a thirteen per cent solution, of which seven and a half parts are added to one thousand of emulsion. Saponin has the advantage of being of definite composition and is obtained from quillaia as well as from soap bark, *Saponaria officinalis*. On the other hand the bark contains sapotoxin and tannin and the latter has obviously some hardening action on the gelatine, while the slight color of the brown doctor when added in the above ratios is not sufficient to cause trouble. The purpose of this addition is to make the emulsion flow well and prevent " comets " in coating.

As regards the alcohol, one cannot use ethyl alcohol, considering the present duty on the same, nor is there any necessity to do so, as pure methyl alcohol, often called Columbian spirits, or acetone, is quite satisfactory.

Eder[2] has given a long dissertation on various additions that have been made at various times to emulsions, but nine-tenths of these are merely of historical interest and either utterly useless or even prejudicial in practice.

Sometimes a soluble bromide, or hydrobromic acid, is added to an emulsion, this being an heirloom from the early days when a clean-working emulsion was practically an exception. The practice has fallen to a great extent into disuse, except possibly for transparency and paper emulsions, but the additions to the latter are dealt with in another chapter. If hydrobromic acid be used, there is probably enough lime left in the emulsion from the washing water to neutralize it, so that actually calcium bromide must exist in the emulsion. The purpose of the addition of the bromide is, of course, to prevent fog in development and also with the idea of keeping the plates. This it may do, but if added in anything like large quantities it certainly slows the plates, that is increases the inertia of the plate with normal time of development. Eder recommended the addition of from one-tenth to three parts of potassium or ammonium bromide per one thousand, the larger quantities being for a foggy emulsion. As regards the hydrobromic acid, a normal addition is five parts of one per cent solution of hydrobromic acid per one thousand. This works out to a ratio of 0.005 per cent of true hydrobromic acid gas, which is probably a negligible quantity.

Sometimes an addition of glycerine is recommended, especially for film and paper emulsions, in order to keep the paper or film supple; but this is a dangerous trick, as glycerine is hygroscopic and may eventually cause trouble. If such an agent is required, it is far better to use golden syrup (cane sugar syrup), about 6.5 ccm per liter. This is not as hygroscopic as glycerine; but it is better to avoid even this, if possible.

An addition of from 0.1 to 5 g of sodium carbonate per liter has been recommended as giving more details in the shadows and making the plates faster, and small additions of ammonia or potassium carbonate have also been suggested. These are dangerous and not likely to improve the keeping power of the plates.

As regards antiseptics, it is an open question whether they are of any practical value, as probably they are entirely lost in the drying process. Phenol is used in the ratio of five parts per one thousand. With regard to thymol, about 0.25 parts dissolved in alcohol is the normal quantity.

One method of treating the gelatine for emulsions, which may be considered as an addition, is unique, the basis being presumably some antiseptic and hardening action. In this case 6.5 per cent of the total gelatine employed was used in mixing and the remainder added after washing the worms, and this was treated as below. A tincture of myrrh was made by digesting one hundred parts of coarsely powdered gum myrrh in one thousand of alcohol for a week, and then filtered. One per cent of this tincture was added with constant stirring to water, and the gelatine soaked in this for an hour with an occasional stir. The water was then drained off and the gelatine added to the melted emulsion. The gelatine had a faint milky appearance and smelled quite strongly of myrrh; but there was no opalescent appearance on the negatives. This was tried out for some considerable time by the writer, but as no particular virtues seemed to be conferred on the emulsion that could not be obtained by the more simple addition of chrome alum, it was abandoned.

MATT EMULSION PLATES. — For some work, particularly stereoscopic, a matt-surface emulsion is a great advantage; it is also used for negatives to facilitate retouching. This may be easily attained by the addition of any finely divided powder, provided it has no action on the silver halides, and is fairly translucent and colorless. Infusorial earth (kieselguhr) or precipitated silica would answer these requirements; powdered glass being also used. Obviously also starch, as used with matt papers, can be used. Rice starch, because it has the finest grain, should alone be used. The exact quantity will depend to a great extent upon the desired result, but the following has been successfully used for transparency plates:

Rice starch	25 parts
Water	250 parts

Heat with constant stirring to 70° C. (158° F.), allow to cool, and stand all night. Heat the next day to the same temperature and add:

Gelatine	25 parts

Stir till this is dissolved, strain through fine linen and add to one thousand parts of emulsion. Barium sulphate may be precipitated in the gelatine solution, but it is not so convenient in practice, as the sodium chloride or nitrate has to be washed out. It gives a finer matt surface to the film, but when dry is too translucent.

It is essential that the matting material be in as fine a state of comminution as possible and as nearly as possible with particles of like size. This latter can be attained by sifting or even elutriation.

It may be useful to recall Tappen & Rekaschow's analyses of some commercial plates, as follows:

Make	*A*	*B*	*C*	*D*
French	0.4373	7.80	46.00	54.00
English	0.4246	8.30	41.44	58.56
English	0.4406	8.65	41.93	58.07
English	0.4770	9.52	41.64	58.36
English	0.5373	8.19	43.22	56.78
German	0.4838	8.74	40.50	59.50
German	0.4323	8.74	40.19	59.81
Austrian	0.6272	8.03	43.44	56.56
Austrian	0.5121	7.87	42.91	57.09
Austrian	0.3465	9.59	36.38	63.62

A is the weight of emulsion in grammes per 100 qcm. *B* is the quantity of water expressed as a percentage of the emulsion. *C* is the percentage of silver halide in the anhydrous emulsion. *D* is the rest calculated as gelatine. From this it will be seen that, excluding the last plate which is obviously exceptional, the quantity of emulsion per 100 qcm is, as a mean, 0.43724 g (about 2.821 g per 100 square inches), and this contains 7.5 per cent of water, 42.6 of silver halide and 50 per cent of gelatine, or a ratio of gelatine of 1.3 to 1 of halide.

As regards the total bulk of the emulsion, this should always be constant and enough water should be added, after all other additions have been made, to bring to bulk. The most convenient plan will be found to base the total bulk on the weight and not the volume of the emulsion, and if the crocks be numbered, as has already been suggested, and a list of their weights kept in a prominent place in the filtering room, it is very easy to place the crock on the platform of a weighing machine and bring up to the standard. This is far better than measuring, as this is always a sloppy matter.

Filtration of the emulsion is an important and necessary operation. One may adopt for commercial work one of two plans, both depending on the creation of a partial vacuum. Which is chosen will depend mainly on the bulk to be filtered.

In the first plan a wide-mouthed bottle is required, fitted with a good bung or rubber stopper, pierced with two holes, through one of which passes a glass or metal pipe connected by suitable stout-walled, non-collapsible rubber tubing with an ordinary brass aspirator screwed on to a water supply. Through the other hole passes a silver tube, one end of which reaches to within an inch of the bottom of the bottle, the other end being flared out into a funnel over which is stretched the filtering medium, the funnel being placed close to the bottom of the crock full of emulsion. This is shown in Fig. 9, in which *B* is the bottle, preferably provided with a tap at the bottom, *A* is the tube leading to the aspirator, *C* the crock full of emulsion with the silver funnel tube *F*. An enlarged sketch of the funnel is shown in Fig 10, in which *F* is the body of the funnel, the lower outside edge being straight with a groove *GG* cut in it, which makes it easy to fasten the filtering medium on. The diameter of the funnel may be about four inches, and the height about the same, tapering off into a half inch silver tube. One has here the weight of the emulsion in the crock added to the pressure of the air, which naturally helps in the filtering. The idea of leading the pipe in *B* close

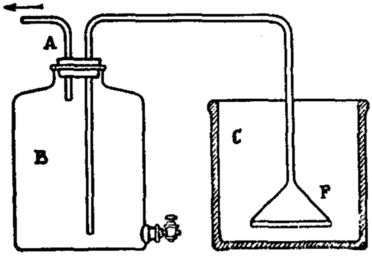

FIG. 9

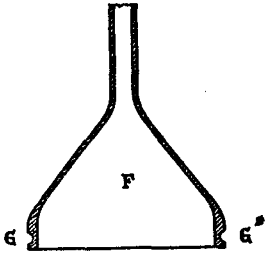

FIG. 10

to the bottom is to avoid the formation of air bubbles. The filtered emulsion can be drawn off from the tap into a pitcher or jug, or a number of bottles may be provided, and each when full carried to the coating machine, in which case the tap at the bottom should end in a drawn-out pipe to enable it to be connected to the emulsion trough of the coating machine.

In the other method, one of the commercial stoneware filter jars is used, which is provided with a ground-in perforated top, on which the filtering medium can be laid. The lower vessel is connected by the usual plug with a vacuum pump, which will be found more efficient than an aspirator. This lower vessel can also be provided with a tap to draw off the filtered emulsion. For small experimental batches, an ordinary Buchner funnel and filtering flask will be found quite satisfactory, if connected with an aspirator.

Other arrangements have been suggested in which the emulsion is forced through the filter by air pressure exerted above the emulsion. The arrangements described above for filtration by vacuum are preferable, as any air bubbles formed in the filtered emulsion rapidly find their way to the top and are broken.

As regards the actual filtering medium, some manufacturers prefer a double thickness of Canton flannel, claiming that this is thoroughly efficient. A more perfect medium is wash leather. If this be used it should be well washed first with soap and water, treated with petroleum ether or gasoline to free it from grease, and hung up to dry. This treatment makes the leather harsh and stiff, but it can be well suppled by washing in warm water just before filtering. After the leather has been once cleaned it is always ready for use, and only requires a thorough washing in warm water after use and then in distilled water and drying.

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[1] *Jahrbuch*, 1906, **20**, 16.
[2] *Phot. Korr.*, 1908, **35**; *Jahrbuch*, 1909, **23**, 371.

CHAPTER X

Coating Plates

As a rule the glass for dry plates is cleaned with the aid of machines in which the glass is fed in either on its edge or on the flat, and scrubbed with revolving brushes with soda lye, then with clean water and finally with distilled water. Some machines are also provided with a further arrangement which applies a substratum, the purpose of which is to make the emulsion adhere well. Machine cleaning is an absolute essential for commercial work.

For small experimental batches hand cleaning is quite efficient, and although a ten per cent solution of carbonate of soda, ordinary washing soda, may be used, the best cleaner is Carey Lea's bichromate mixture:

Potassium bichromate	100 g
Sulphuric acid	100 ccm
Water	1000 ccm

Add about 200 ccm of the water to the bichromate and then, slowly, the acid; the temperature of the mixture will rise considerably, probably high enough to dissolve the salt; then add the remainder of the water.

Care must be taken in the use of this, as it attacks the hands. The best way to use it is to fill a dish with the solution and immerse a sheet of glass. Scrub the surface with a nail brush, then, with the aid of a stick, turn the glass over and scrub the other side. Procure a piece of board and nail on it a strip of carpet, and place the board in a sloping position under a tap. Lift the glass from the dish and with the left hand, which should be provided with a rubber glove, place the glass on the board with the water running and scrub the one side and then the other, then rinse thoroughly under the tap and put in the rack to drain.

The older substratum was a solution of potassium or sodium silicate, water glass, but this is apt to fog the plates. A much better solution is

Gelatine	5 g
Chrome alum	0.5 g
Water	1000 ccm

Some use this double strength with the addition of ten per cent of alcohol. The plates should be dipped bodily into this solution, at about 20° to 25° C. (68° to 77° F.), and then stacked in a rack to drain and dry. The coating left on the glass is extremely thin, but quite sufficient to make the emulsion adhere well.

For experimental work there is nothing better for coating than a small china or stoneware teapot, with a spout that comes from near the bottom, or an invalid's feeding cup may be used, one of the round shape. It is possible to obtain teapots with an inner strainer, which is very convenient, as one can tie the filtering medium round this. For years the author used a half pint stoneware teapot, for which a solid silver strainer was made of the shape shown in Fig. 11. The diameter of the top was two inches and it was flared out so as to form a solid seat, which fitted on the ledge where the usual lid rested. The little groove at the bottom enabled one to secure the filter cloth firmly. The depth of the strainer from the top to the bottom was three inches, and thus it reached to within about an inch of the bottom of the pot. When starting to coat, the emulsion was poured into the strainer till the pot was full, and any emulsion drained off the plates was run back into the strainer.

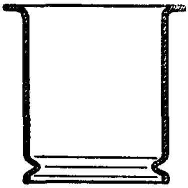

FIG. 11

Coating the plates is merely a matter of experience, and it should be practiced in a bright light till the trick is learnt. Some operators judge of the thickness of the coating by looking through it at an electric lamp under a transparent safelight, and judge of the quantity of emulsion from the visibility of the filament of the lamp; others merely judge by the thickness of the film at the edge of the plate. A pneumatic bulb should always be used, as this obviates the possibility of touching the glass with the fingers. When an exact quantity of emulsion is required for a given plate surface, a graduated pipette must be used. A convenient temperature for coating is about 35° C. (95° F.).

The glass should be stacked in a close pile against the wall or other support, and the pneumatic bulb squeezed and pressed into contact with the back of the plate in the center. This enables each plate to be lifted without touching with the fingers. The plate should then be held in a horizontal position, and enough emulsion poured onto the center to cover about a quarter of the area. The glass should then be tilted to the right hand top corner, then to the left hand top corner, then to the bottom left hand corner, and finally to the right hand bottom corner, and excess of emulsion drained off here by tilting the glass to an angle of about thirty degrees. It is as well to perform this operation over a large dish so as to prevent any spilling of the emulsion on the bench.

The coated plate must be placed on a levelled slab to set, and while for a plate or two a sheet of plate glass may be used, it will be found much more convenient to have a proper setting box. The size of this box will vary according to the number of plates to be coated, but as a rule one large enough to take six whole plates, six and a half by eight and a half inches, will be ample, so that, allowing for a little room between the plates, eighteen by twenty-one inches is large enough for the actual setting table, plus the opening described later. The top should be for preference iron plate one-sixteenth of an inch thick, the depth of the box may be three inches, and the sides can be made of stout zinc; but the whole should be water-tight, and provided with levelling screws. At one end should be a square funnel-shaped aperture, as in Fig. 12, with about a three-inch slot. This enables the box to be filled with cracked ice, and, then, if it is filled up with cold water to just above the level of the setting table, the latter will be kept cold enough for any number of coatings.

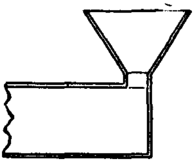

Fig. 12

As soon as the film has well set, the plates should be placed in racks, with not less than an inch between the plates. The usual draining rack is a delusion and a snare, as the grooves are too small and touch too big a surface of the plate. It is far better to make a skeleton frame of wood (as metal must not be used) with small cleats on the sides, and place the plates face up. This should be fitted with a removable lid, which completes the box. This is shown in Fig 13. The actual dimensions of one used for 6½ x 8½ plates were as follows: $AB = 7$ inches, $BC = 8\frac{3}{4}$ inches, $BD = 7$ inches. The cleats at the sides were, as shown in Fig. 14, made of wood one-quarter inch thick and one-half inch wide, with three-quarters of an inch between the cleats. It is very easy to place the plates face up on these little shelves without touching the sides, and as soon as the six plates are in position, the lid is clapped on, and the next box filled in the same way. As four were used, they made, when pushed close up to one another, a long box, through which a good current of hot air was driven by one of the little hairdressers' hot-air fans. This fan should be arranged at such a distance from the edge of the first box that the air travels fairly equally over all the plates; with the writer's fan this distance was nine inches. The temperature can be easily controlled and can range from 35° to 45° C. (95° to 113° F.) Too much heat is not advisable, but it should be kept constant as far as possible, otherwise drying marks make their appearance, which are distinctly visible on development.

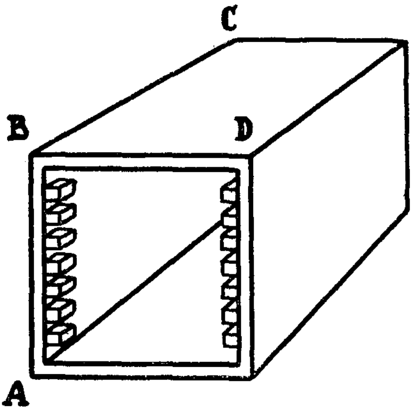

Fig. 13

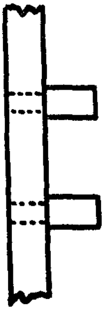

Fig. 14

For commercial work the plates are always machine-coated and various patterns of machines have been patented. These machines may be divided practically into two parts, the actual coating mechanism and the setting table.

It may be noted that as a rule the small sizes of plates are coated in multiple, that is to say, the glass is larger than the actual size of the plate. For instance, 4 x 5's are usually coated as 8 x 10, the quarter plate 3¼ x 4¼ as the whole plate 6½ x 8½, and the English lantern plate, which is 3¼ x 3¼, as 6¼ x 9¾; in fact the whole plate is usually the smallest size that is actually coated as such. For the smaller size plates, also, thinner glass is used. The cleaning and substratuming of the glass has already been dealt with. In some cases it is the practice to warm the glass slightly, this being said to prevent the occurrence of smeary marks; but it has been found that if the glass be stored in the coating room for a little time prior to the commencement of work there is no danger from this source. These smears are due to too rapid a setting of the emulsion before it has time to even itself out, but this can always be obviated by slightly increasing the temperature of the emulsion.

J. H. Smith[1] introduced a machine, shown partly in Fig. 15, of which the following are the principal details. The glass plates *AA* are stacked on the shelf *BB* and fed on between the guides *CC,* on small rollers *DD* on an endless belt *E;* the guides being adjustable to the various widths of the glass by the handle *F*. One, two or three lines of plates can be coated at once, and the greatest breadth permissible is 60 cm. The endless belt, on which the plates lie, is actuated by the grooved pulley *G* and hand wheel *H,* or by power. The power required was said to be small so that a child could work the machine.

The front endless belt *E* carries the plates under the coating apparatus *J,* which is separated by a

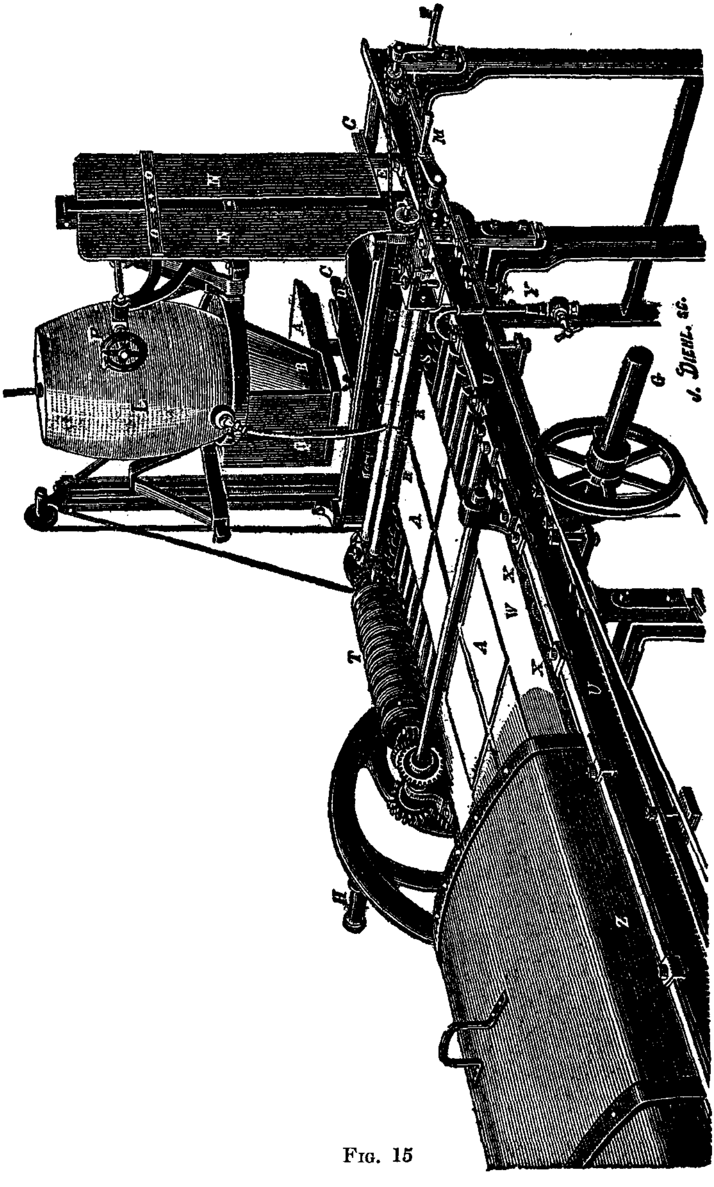

Fig. 15

division *K* into two parts. The emulsion is stored in the vessel *L,* which should be covered with felt to hold the temperature up. This is practically a Mariotte's bottle and thus delivers the emulsion regularly, no matter what its level. This vessel can be raised or lowered by the handle *M*. The quantity of emulsion in cubic centimeters, delivered per minute at any position of the vessel, is read off by the pointer *O* on the scale *NN*. By turning the handle *P,* the vessel can be tilted so that the last drop of emulsion can be used.

The emulsion runs through the pipe *Q* into the rear section of the coating trough and passes through a slit into the front section. The requisite quantity of emulsion per minute is determined according to the width and speed of the movement of the plates and the pointer set on the scale *N*. It was stated that an accuracy of from one to two per cent could be obtained. In the front section of the coating trough the emulsion is level and flows over a lip in an even stream, equal in breadth to the plate to be coated. Only about fifty grams of the emulsion was left in the trough at the end of the run. The emulsion flows over the edge of the trough onto a bent scraper *RR* which swings on an axis and thus adjusts itself to the thickness of the glass. Under the coating trough is another one *S,* which catches any emulsion that may overflow or run between the edges of the plates. As soon as the plates are coated, they are slightly separated from one another by means of the wheels *R,* no matter what size they may be. The plates then pass into the long cooling trough *UU,* and are carried by the horizontally driven rollers *VV,* finally passing on to an endless belt *W,* which is carried by a series of brass rollers *X*. *Y* is a supply pipe for cold water, and at the opposite end of the table is an outlet, that can be regulated so that the rollers, which are covered with felt, are kept wet. The travelling band is also kept constantly wet with chilled water, and the emulsion sets quickly. This arrangement is stated to be so efficient that even in summer no ice is required. The whole length of the setting table is provided with removable metal covers *Z* to prevent the access of dust and light. The best speed of the driving wheel was stated to be thirty to forty revolutions per minute, equivalent to a plate speed of two to five meters per minute. The maximum production was forty 18 x 24 cm plates per minute.

J. Cadett patented [2] a machine, the coating end of which is shown in Fig. 16, and as will be seen consists of a number of silver pumps, and the trough is shown in Fig. 17. The chief advantages of this machine are said to be the delivery of exactly the same quantity of emulsion irrespective of the height of the same in the trough or the speed of the machine, and the absence of air bubbles or sediment, as the intake is always below the top of the emulsion and sufficiently far from the bottom of the trough.

The emulsion flowed first onto the silver plate corresponding in length to the width of the plate to

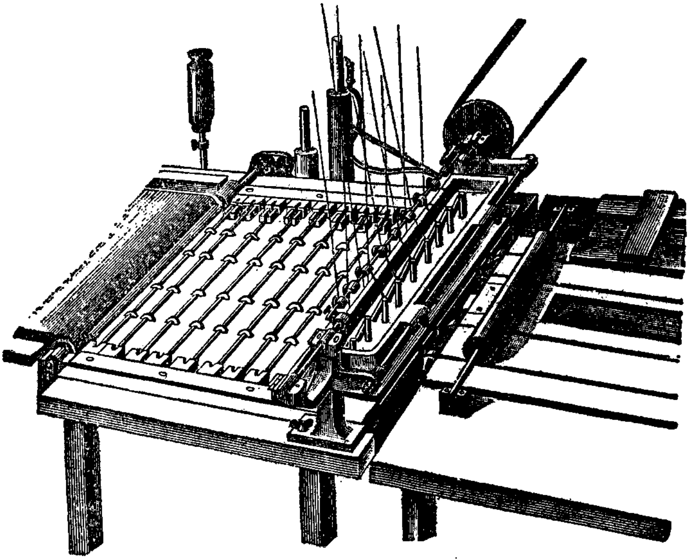

FIG. 16

be coated, the number of pumps in operation being adjusted to this width. In front of this silver plate was a silver roller, hanging on two cords, so as not to touch the plates, yet serve to distribute the emulsion evenly. Unevenness of the glass was also nul-

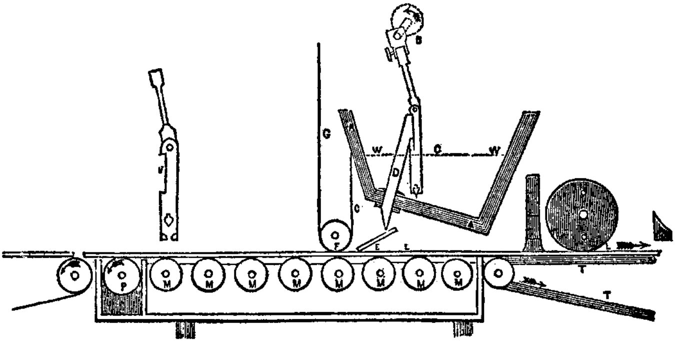

FIG. 17

lified to a certain extent, as the cylinder was broken in the middle and joined by rubber, and also supported by a third belt in the middle, as shown in Fig. 18, to prevent sagging. This cylinder was constructed of paper-thin silver and had, therefore, no material weight. In Fig. 17 *AA* is the water-jacketed emulsion trough, *B* the eccentric which drives the pump *C, D* the outlet pipe, *E* the silver plate over which the emulsion flows and *F* the distributing silver cylinder or roller, the distance of which from the glass is determined by the cords *G*. *LL* are the plates to be coated, *M* the rollers in a warm water trough and *P* a transfer roller, which revolves at somewhat greater speed in a trough of its own, and transfers the plates to the endless belt the beginning of which only is shown, and *WW* is the level of the emulsion in the trough.

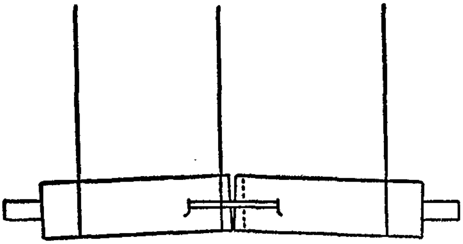

FIG. 18

B. J. Edwards patented[3] a coating machine, shown in section in Fig. 19, which has been used very successfully by the writer. *A* is the emulsion, *B* the coating roller, *F* the endless belt, which was of fine rubber-faced four-ply canvas three millimeters thick. *K* is a trough filled with hot water, through which ran an endless carpet with thick pile, that cleaned the backs of the plates, which were transferred to the endless belt *L*, which was of woven copper wire. This belt passed over a slate bed *NN*, under zinc troughs *R*, filled with ice. The wire band on the chilling table travelled slightly faster than the band of the coating end, so that the plates were automatically slightly separated.

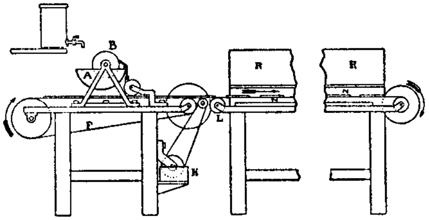

Fig. 19

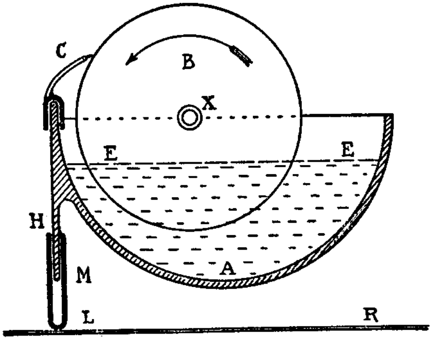

Fig. 20

The special feature of this machine was the coater, which is shown in section in Fig. 20. *A* was a solid silver trough, the level of the emulsion being *EE*. The coating roller should be preferably a turned glass cylinder, though silver might be used. This roller turned in the direction shown by the arrow. This cylinder must not be plated, as the plating is very soon worn off by the action of the scraper, and for this reason glass is even preferable to pure silver, though a little more trouble to obtain with a true surface, which need not be polished, fine matt acting well. This cylinder, working in ball bearings, has its axle prolonged at one side into a series of coned wheels, by means of which and a round belt working in conjunction with a lower cone series, various speeds of revolution can be obtained. *C* is a pure silver curved piece which carries at its end a strip of pure red rubber, of the shape shown in Fig. 21 *D,* which actually scrapes the emulsion off the cylinder. This curved piece springs onto the front wall of the coating trough, and this front wall is prolonged at the bottom into the piece *H,* which also carries another spring piece *M,* which clips a piece of well-washed nainsook linen that actually delivers the emulsion to the glass. The shape of the rubber strip is shown half size in Fig. 21 *D* and the edge *S* bears slightly against the roller *B*. This strip is clipped by pins and flat headed screw nuts, the ends of the pins being soldered into and flush with the face of the spring clip so as not to offer any resistance to the flow of the emulsion. The length of the strip obviously was that of the

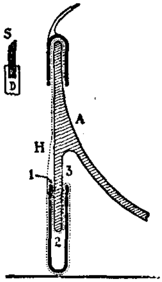

Fig. 21

plate to be coated and the width of the linen was the same.

The method of fastening the linen is shown in Fig. 21 *B*. The linen, shown as a broken line, was started at 1, brought round 2, 3 and 4 up the face of the trough wall and over the top, where it was clipped tight. At first there is nearly always some slight difficulty in obtaining an even flow of the emulsion down this linen, but this could be at once evened out by passing the finger across it, so that only a plate or so was lost. The faster the cylinder revolves the more emulsion is delivered to the glass. The plate travel was from right to left of the diagram.

The rubber feeding-on band was four and a half feet long and eighteen inches wide; the carpet band being five feet, nine inches long. The copper wire band, for carrying the plates, was eighteen inches wide; the length of the slate bed was twenty-seven feet, which was found ample for all purposes. The wire band ran over rollers at each end, being actuated by an endless leather belt passing round a grooved wheel at the end of the setting table, opposite the coater. Under the machine were brass rollers on adjustable arms, which kept the band taut. Fig. 22 shows a section of this setting table with one of the ice troughs in position. The walls of the trough were strengthened by cross pieces and each side was provided with a tap to run out the melted ice-water. Each trough was also provided with a cover. The actual measurement of each trough was three feet long, ten inches in depth at the sides and six inches at the center, the width being naturally that of the machine. The frame work of the whole table was wood, that of the coating machine cast iron.

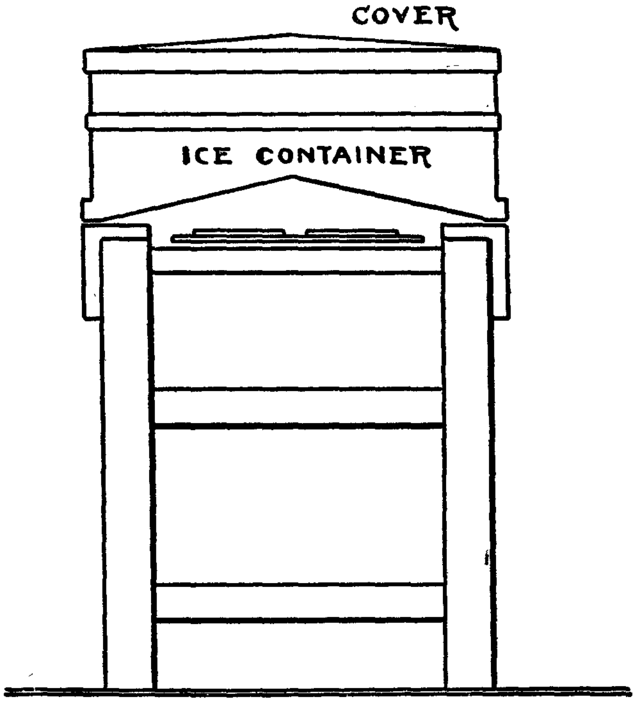

Fig. 22

It is unnecessary to deal in detail with other machines, as reference can be made to the various patents by those interested. A. L. Henderson[4] used a tube with a slot in it. Tubes of various lengths were used for the different sizes of glass or a long one with adjustable rubber stoppers at each end, these being on the ends of rods to enable them to be pushed in or out. This has also been successfully used by the writer, but it should be noted that the length of the slit must be slightly less than that of the glass, as the emulsion spreads a little. J. Gaedicke [5] patented the use of two glass or ebonite plates between which the emulsion flowed by capillary attraction, the upper end of the plates being flared out to form a funnel as in Fig. 23. Kattentidt used [6] a flat vessel which was supported on a warm water bath, Fig. 24, the front of the vessel being provided with an adjustable plate *L*, by means of which the width of a slit, which was covered with linen, could be adjusted.

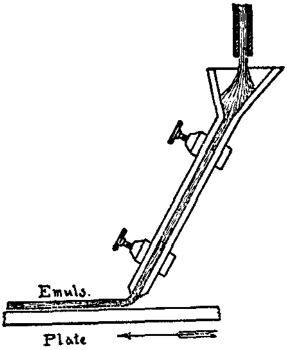

Fig. 23

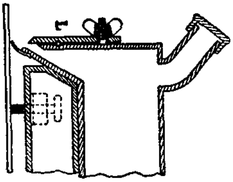

Fig. 24

It is important, particularly with film and paper coating machines in which the emulsion is picked up from a trough, that the level of the emulsion be kept constant and the surface free from bubbles. Various devices have been suggested for this purpose. The writer has successfully used a constant level float as shown in Fig. 25, which is drawn to scale. It consists of an outer box *ABCD* of solid silver one-sixteenth inch thick, three inches from *A* to *C*, three inches from *A* to *B*, divided at *EE′* by a silver plate with a central aperture of one-half inch diameter. *F* is a small circular drum, made of silver one-thirty-second inch thick, two inches in diameter and one inch deep, completely soldered up, which forms the float. To the top of this float is soldered a thin rod *R′* which passes through the hole *H*, which is provided outside with lugs *LL*, for the rod to work smoothly in. To the bottom of the float is also fastened a rod *R*, working through a hole *H′* of one-half inch diameter against which the plate *G* fits, the upper face of *G* being perfectly flat, seven-eighths inch in diameter, and one-sixteenth inch thick. *M* was a half-inch pipe let into the side of the box, through which passed a glass tube connected with the emulsion stock pot. *M′* is a similar size pipe, connected with the emulsion trough. The emulsion enters through *M*, fills the

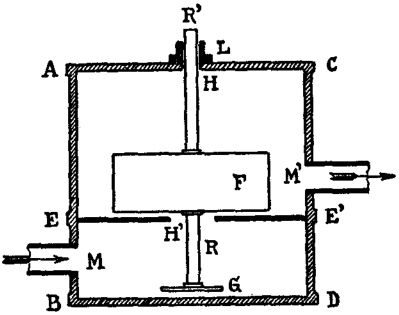

FIG. 25

lower chamber *EBE′D* and thence flows through *H′* into the upper chamber *AECE′*, raising the float *F*, and out through *M′* into the trough. As soon as the emulsion has here attained the height above *EE′* equal to the length of the rod *R*, the supply of emulsion is cut off, while as soon as the level sinks in the trough, the float *F* sinks and opens the hole *H′*, allowing more emulsion to flow through. The box unscrews at *EE′* and *AC* to allow for cleaning, and the plate *G* also unscrews so that the float can be entirely removed.

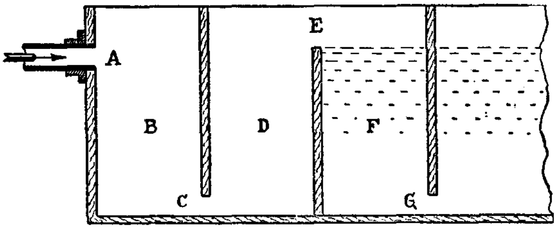

Fig. 26

In order to avoid the formation of air bubbles it is very usual to make use of a weir arrangement, as shown in Fig. 26 in section. The emulsion enters through *A* into *B*, flows through the slit *C* into *D* and over *E* into *F* and out through the slit *G* into the trough. It is obvious that any bubbles that may be in the emulsion tend to rise to the top of *B* and *E* and do not gain access to the trough. Naturally this also acts as a constant level arrangement as the emulsion does not rise above the level of *E*. The slits *C* and *G* are the full width of the trough.

It may be pointed out that bubbles will sometimes be formed, even when the greatest care is taken, in the trough itself, by the passage of the celluloid into the emulsion. These need not be feared, as if a stock of spills of filter paper is kept at the side of the coating trough, they can generally be broken by touching them with a spill or led to the edge of the celluloid, and although this makes a mark in the coating, this mark will disappear in the run up of the celluloid.

It has been recommended more than once in these pages to use rubber connections and it may obviate any doubt on this point if it be stated that pure black rubber has apparently no action on the emulsion. Naturally one will limit its use as much as possible on the other hand, because of the possibility of tubes of this material not being properly cleaned inside; but short lengths can be used without fear. Hard rubber also seems to be without action.

When it comes to the coating of film and paper one has a totally different proposition to deal with as compared to glass, for the former are flexible and will not of themselves lie flat, save cut sheet film.

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[1] *Eder's Jahrbuch*, 1892; 385, and 1893; 97.
[2] *Eng. Pat.* 9,886, 1886; 13,725, 1887.
[3] *Phot. News*, 1884, 541; *Phot. Archiv*, 1884, 304.
[4] *Eng. Pat.* 424, 1885.
[5] *D. R. Pat.* 59,392; *Eder's Jahrbuch*, 1893, 169.
[6] *D. R. Pat.* 51,645.

CHAPTER XI

COATING CUT SHEET AND ROLL FILM

BY the term " cut sheet film " is meant the thicker celluloid films, about ten one-thousandths of an inch thick. This is usually obtainable commercially in sheets that measure approximately 50 by 21 inches, but after trimming off the edges, which are usually irregular and slightly cockled, the working area is 48 by 20 inches. These sheets may be cemented together on the narrow ends so as to form a continuous sheet, but the thickness is so great that any number make a very unmanageable roll, and they are, therefore, usually cut before coating. If it is desired to join them together so that they may be coated on the film machine like the thinner film, the following cement may be used:

Celluloid	10	g
Amyl acetate	330	ccm
Acetone	670	ccm

Clamp a steel straight edge right across the film and with a sharp penknife or safety razor blade scrape the surface of the celluloid for about three-eighths of an inch, on the upper side of one sheet and the lower side of the other. With a camel's hair brush, cut down so as to give short hairs, paint the two scraped surfaces with the cement and bring into contact, rub into intimate contact with a smooth hard surface, such as the rounded edge of a paper knife, and preferably clamp down between two steel plates at least three-quarters of an inch wide and one-sixteenth inch thick, so as to prevent the edges from springing apart. In coating, the butt of the joint must be against the travel of the film in the machine. If this be reversed, the little ledge formed by the edge of the film causes streaks in the coating.

If the celluloid is coated in the sheet, it is better to cut it up into smaller sizes, preferably 20 by 16, which is a size easy to handle. Plate glass of this size should be obtained, one-quarter inch thick, and the sharp edges ground off. After thorough cleaning and substratuming it should be coated with the following:

Hard gelatine	58 g
Golden (sugar) syrup	58 g
Glycerine	86 g
Chrome alum	0.8 g
Water to	1000 ccm

Soak the gelatine in the water for thirty minutes, melt at 50° C. (122° F.), and filter; then add the syrup and glycerine, both of which should be weighed, and finally add the alum, dissolved in about 50 ccm of hot water, with constant stirring. Allow 250 ccm for every 20 x 16 sheet of glass, and when thoroughly set, allow to dry, which may take three or four days. Actually, of course, the coating never dries, but forms a tacky film to which the celluloid adheres firmly.

To lay the celluloid down it is advisable to use a heavy roller, preferably of brass or iron, from two to three inches in diameter, and two to three inches longer than the width of the plates, with a handle at both ends. This roller should be covered with white felt, thin piano felt, which should be cut in strips two inches wide and wound spirally around the roller and fastened on with glue. Over this felt should be wound in the opposite direction strips of chamois leather. Obviously a printer's velvet-covered roller may be used. The point is to have as smooth a surface as possible and the roller should be heavy enough to ensure intimate contact between the celluloid and the tacky plate without the operator having to put any weight on it.

The glass should be laid on a sloping board, covered with thick felt, and the upper edge of the board should end in a steel straight edge, which should be just about one-quarter of an inch above the board. If the glass and celluloid are cut straight, both may be butted up against this edge, and the roller, if placed at the top on a flat piece, can be easily rolled down over the celluloid, forcing it into perfect contact. Such a board is shown in section in Fig. 27, in which *A* is a wooden stop to prevent the roller from falling off the little table *AB*. *C* is the steel straight edge, and *D* the sloping board. Of course, it will be understood that such an arrangement is not actually necessary, but in practice it has been found to facilitate the work. Celluloid thus mounted can be treated exactly like glass plates and coated on a plate-coating machine.

To strip the celluloid, it is advisable to place the plates, after removal from the drying room, in a cool damp place and leave till quite cold, and then pass the end of a thin ivory paper knife under one side so as to raise the celluloid for about an inch. It can then be stripped with a gentle even pull. If force is used, static electricity is generated and makes itself apparent on development as fog, and this is particularly noticeable if a stoppage is made in the stripping, as a line of denser fog. How to completely prevent static is not known, but it is much lessened by leaving the plates to get thoroughly chilled, and stripping in a damp room.

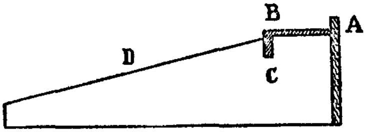

Fig. 27

A gelatine emulsion has the greatest objection to adhere to celluloid. It will do anything but that, unless a substratum is used. Various solutions have been suggested, such as sodium silicate, invert albumen, etc. The virtue of the first probably lies in its alkaline nature, which slightly saponifies the extreme surface of the celluloid, but it is apt to fog the emulsion. Invert albumen is a trouble to make, and it is an open question whether its efficiency is not due to the solvent as much as the albumen. Still for those who want to try it, the following is the best way of making it:

Albumen (white of egg)	1000 ccm

Beat to froth and add:

Glacial acetic acid	15 ccm
Water	30 ccm

Allow to stand for an hour or till liquid, then filter. Add an eight per cent solution of caustic soda, drop by drop, stirring continuously till the solution thickens, then allow to stand for thirty minutes, when it should be a solid mass. Break up and wash like an emulsion for two hours. Then add a mixture of equal volumes of ethyl and methyl alcohol to make 10,000 ccm. Instead of the egg white, dry albumen may be used and dissolved in water, about 150 g being equivalent to the 1,000 ccm of the fresh albumen.

While the term substratum has been used in connection with celluloid it must be recognized that its action is not the same as that of the chrome gelatine substratum for glass, which actually does form an infinitely thin film of cementing material. In the case of celluloid, the action of the substratum is rather an etching of the surface. This etching is not apparent to the naked eye, but it can be seen microscopically and also detected by the greater readiness with which a basic dye solution will penetrate such a surface compared to an untreated surface.

An early form of substratum was:

Celluloid	2.5 g
Ether	100 ccm
Alcohol	900 ccm

This was not very satisfactory. The following is preferable:

Ether	625 ccm
Acetone	375 ccm
Glycerine	25 ccm

The objection to this is the ether fumes which, if an efficient system of ventilation be not installed, form a serious menace to the workmen, and also increase the fire hazard. The substitution of alcohol for the ether is a great improvement but there is danger, unless the drying temperature is rather high and the air very dry, of the surface turning white, or " blushing," as it is called. The most efficient coating the writer has used is:

Gelatine	5 g
Glacial acetic acid	50 ccm
Water	10 ccm
Methyl alcohol	1000 ccm

Soak the gelatine in the water and acid and melt to 55° C. (122° F.), then add the alcohol, heated to the same temperature, slowly with constant stirring. For cellulose acetate film, half the alcohol should be replaced by acetone. The above is suitable for all celluloid film, whether coated on the flat or roll;

but for cut sheet film the following also may be used:

Pyroxylin	0.5 g
Gelatine	0.5 g
Glacial acetic acid	33 ccm
Methyl alcohol	1000 ccm

Dissolve the gelatine and pyroxylin in the acid by heat and add the alcohol.

To substratum the cut sheet film, fastened on the tacky glass, it is sufficient to use a good sized ball of absorbent cotton wrapped in Canton flannel. Damp the surface of the pad with the above solution and lightly pass over the celluloid. Vigorous rubbing must not be resorted to. This may cause the surface of the celluloid to appear smeary and streaky, but no notice need be taken of this, as the marks will not show when coated with emulsion.

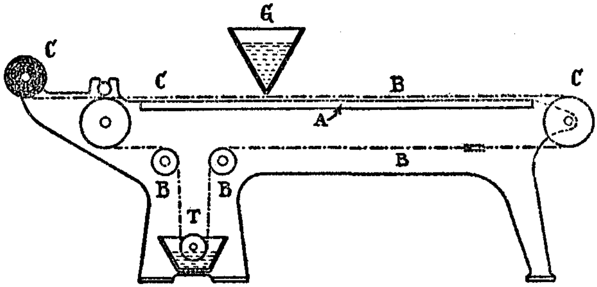

FIG. 28

It has been suggested that it is possible to coat roll celluloid on the flat, and the design of the machine is shown in Fig. 28, in which *C* is the roll of celluloid which is squeegeed between the large and small rollers to an endless band passing over the table *A* under the coating trough *G*. The endless band passes through a trough *T* in which is ice-cold water, which chills the belt and at the same time causes adhesion of the celluloid to the same. This is introduced as a warning against an utterly impracticable practice, as the writer can aver from experience. Adhesion can be obtained between the band and the celluloid, but as soon as the warm emulsion touches the celluloid one has a glorious crop of bubbles under the latter, and it is impossible to obtain an even coating. As a possible improvement the author tried coating the band, a costly eight ply endless rubber belt two feet wide and fifty feet long, with the adhesive mixture given on p. 183, but it was found that the surface of the belt was not sufficiently flat of itself to permit an even coating, and even when scraped and polished down with benzol, the resultant film was commercially impossible, as the rubber itself wrinkled under the pressure and caused irregularities of coating.

The principle of coating celluloid in the roll is to make it present as even and flat a surface as possible to the emulsion trough and for a sufficient length to enable the emulsion to even itself out. The principle is clear from Fig. 29, in which the distance between the point where the celluloid leaves the emulsion and where it turns from the straight, technically known as the run, determines to a great extent the evenness of the coating. In the writer's experience this should not be less than thirty-six inches, though it naturally depends on the gelatine content of the emulsion, its temperature and that of the coating room. If one considers that the emulsion is usually at a coating temperature of 33° C. (92° F.), it is obvious that with any reasonable thickness of coating there is some appreciable time before it sets. There is thus a constant tendency for it to flow, and the straight run gives it the best chance to even itself out. If on the other hand the celluloid, immediately after leaving the coating trough, be turned over at right angles to its previous path, unless the celluloid be kept under extreme tension there is a great tendency for it to buckle and the emulsion will run into uneven waves.

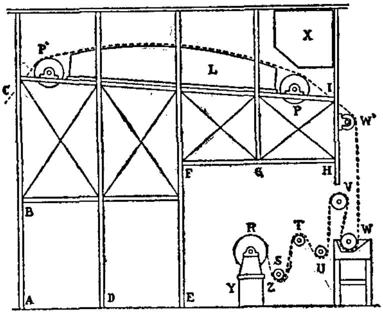

FIG. 29

The type of coater favored by the writer is that shown in Fig. 29. On the other hand by some it is considered that the type shown in Fig. 30 is preferable. Having worked with both types, it may be said that unless the run be made long enough, there is great danger with the latter type of unevenness of coating. The setting surface is much smaller in the latter type, and trouble may thus be later caused, at any rate in the extreme heats met with in America. The setting surface in this type of machine is, of course, dependent on the diameter of the chilling cylinder *C*, and assuming this to be three feet, which is normal, then the actual chilling surface must be only two and one-third feet, which is very close to the danger line. This can be increased by leading the celluloid round a greater arc of the circle, but even under the best conditions it is not possible to utilize more than about 67°, or with the above diameter about three and one half feet, whereas with the other type of machine the setting surface may be from ten to twelve feet or longer if desired. It will be understood that mere setting or gelling of the emulsion is not the only desideratum. It must be thoroughly chilled,

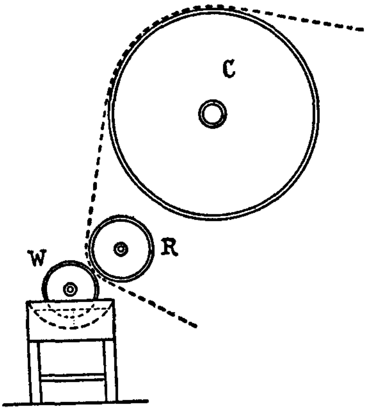

Fig. 30

and the colder it is when it leaves the setting surface, the less chance for it to subsequently melt and run.

In the system of Fig. 30, the so-called wiping system, the roller *W* is usually of somewhat smaller diameter than the other *R*, and revolves in the trough of emulsion in a direction contrary to that of the film or paper travel, thus picking up the emulsion. This pick-up roller can be more or less approached to the surface of the material, so that the emulsion is transferred to the latter by capillary attraction, or if the two rollers are close enough, by actual wiping. The faster the small roller travels and the closer it is to the surface to be coated the more emulsion is applied.

One of the special advantages claimed for this method is that the smaller roller may be slightly shorter than the material, so that a narrow uncoated strip is left at each edge, thus tending to prevent undue curling at the edges during drying. Also, obviously, there is no chance for any emulsion to find its way on to the back of the film or paper. It should be pointed out, however, that if the material is fed to the coating roller in the dipping system as outlined below, the chance of this last trouble occurring is very slight.

The details of the machine, Fig. 29, are as follows: The frame work is two-inch angle iron, and the height of the room is supposed to be twelve feet in the clear. The following are the dimensions: *A* to *B*, 3 ft. 6 in.; *B* to *C*, 6 ft. 9 in.; *A* to *D*, *D* to

E, *F* to *G*, *G* to *H*, each 3 ft. 3 in.; *E* to *F*, 5 ft. 6 in.; *H* to *I*, 3 ft. *P* and *P′* are wood pulleys twelve inches in diameter, slightly crowned in the centers to prevent the belt running off. Between these two pulleys is a suction box *L*, 9 ft. long and 8½ in. in height at the crown, the ends being of such height as to form a straight run from the crown of the pulleys. The top of this suction box is a brass plate, which should be six inches wider than the celluloid to be coated and perforated with one-half inch holes, with one-half inch between their circumferences, along its whole length; but the outside perforations should be three inches on each side less than the celluloid. Over the pulleys and the top of the box should be stretched a belt of white piano felt, about one-sixteenth inch thick, which should be two inches narrower than the brass plate. An idler pulley may be fitted under the center of the box, about three inches in diameter, so as to take up any stretch in the belt, or one of the pulley bearings may be adjustable along the angle iron for the same purpose. This latter plan has the advantage that if the belt stretches unevenly one bearing may be advanced more than the other.

To the side of the suction box should be fitted a strong exhaust fan which, sucking the air through the felt, holds the celluloid down perfectly flat and smooth. It may be stated that with sufficient suction and without the belt being driven, it is possible for a man weighing over one hundred and sixty pounds to hang on the celluloid without being able to move it.

At the top in front of the main frame should be fitted the cold air box *X* which should be provided with a good blower driving the cold air along the top of the box towards *C*. The colder this air is the better.

We have thus far dealt with the main frame and can now treat of the coating end. ***R*** represents the reel of celluloid to be coated, wound in the usual manner on a mandrel which should be provided with wide flanges at each end to keep the celluloid in position. These mandrels should be interchangeable with the receiving end of the dope casting and substratum machine, and should revolve freely in ball bearing sockets. From ***R*** the celluloid, shown throughout by the broken line, is carried under and over the rollers ***S, T, U, V*** to the coating roller ***W;*** thence up the run to ***W′,*** over across the top of the suction box to ***P′*** and thence into the drying room. All the rollers, ***S, T, U, V, W, W′,*** are three inches in diameter, and with the exception of ***W*** may be of brass tubing with brazed-in ends.

The height of the axle of ***R*** may be eighteen inches; that of ***S,*** twelve inches; of ***T,*** thirty inches; of ***U,*** twenty-four inches; of ***V,*** forty inches. The separation between the centers of these rollers may be ***R*** to ***S,*** twelve inches; ***S*** to ***T,*** six inches; ***T*** to ***U,*** eight inches; ***U*** to ***V,*** six and three-quarter inches; all these measurements being between verticals dropped from the axles to the floor. The purpose of these rollers is to keep the celluloid in perfect tension. For the same reason the side pieces carrying the bearings for the celluloid mandrel should be free to rotate on a central pin on the lower table *YZ;* this provides a little side play, compensating for variation in thickness of the celluloid and any slight wandering of the edges.

It is important that the celluloid should hug the roller *W* as closely as possible, so as to prevent any emulsion from creeping in behind and smearing the back. This can be effected by arranging the roller *V* so that its axis is just in a vertical line with the rear edge of the coating roller *W*, or in other words the front edge of *V* should be vertically above the axis *W*. The celluloid thus comes into contact with the periphery of *W* before it has a chance to touch the emulsion and hugs it so tightly that in a continuous run of four hundred feet the emulsion does not creep in more than about one-sixteenth inch. Naturally this depends on the depth to which the coating roller is immersed in the emulsion, and it may be thought advisable to place *V* on bearings, adjustable as to their relation to the axis of *W*, which can be easily done by lengthening the brackets carrying *V*.

The coating trough stands in the hot water box, which is seen projecting from the front of the machine. This water box must necessarily be the full length of the coating trough. It may be approximately twelve inches deep and fitted on one side with a steam or hot water pipe and also a cold water supply pipe, so that the temperature of the water in the box may be regulated. It will be found, as a rule, that this temperature will be from two to three degrees higher than that of the emulsion, in order to hold the latter constant. Both the pipes in the box should be perforated with small holes, so that the water is forced with some pressure into that already in the box, thus mixing rapidly and altering the temperature as rapidly as possible. A waste pipe must also be fitted and the diameter should be generous, at least one inch, so as to carry off the water freely, and prevent its accumulating in the box; this can be fitted at the opposite end to that at which the water enters. A thermometer with bent tube and easily legible scale should be fitted at one side or in the center of the front, and as the range of temperature required is comparatively small, say from 27° to 40° C. the divisions of the scale may be fairly large. The box may be of wood, copper lined; the height from the floor is about twenty-two inches, its width twelve inches.

The actual coating trough may be hemispherical in shape, though the writer prefers one of the shape shown in Fig. 31. Whichever be adopted it should be silver or copper with a sweated-in solid silver lining. The coating roller *W* should also be solid silver tubing, with brazed-in ends. A plated roller here is utterly useless, as the edges of the celluloid are sufficiently sharp to cut through any plating in a very short time. A hard rubber roller may be used or one covered with bakelite or similar phenolic condensation product. The coating trough should have wide flanged edges so as to rest easily on the top of the water box, and a wooden turnbuckle should be provided at each end to hold the trough down, otherwise it may by accident float up, when too much water gets in the box or the emulsion in the trough is too low.

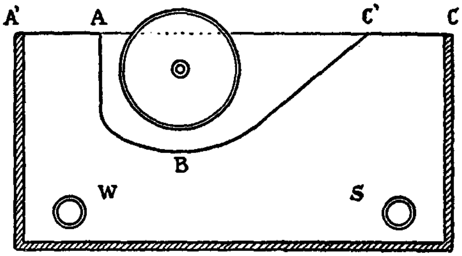

Fig. 31

The dimensions of the trough preferred by the writer, as shown in Fig. 31, are *A′A, C′C,* one and a half inch flanges; the depth *A* to *B* measured vertically above *B,* four and one-eighth inches; *A* to *C,* ten inches. The length will naturally depend on the width of the celluloid to be coated. The depth of the emulsion should be about two and a half inches, though this is not material, as the coating roller can be lowered at will. But it is important that the axle of the roller be at all times well above the level of the emulsion; in practice it will be found that if the roller dips into the emulsion to about half way between the axle and its edge as shown by the broken line, good coating will be secured. If the roller is lowered so much that the axle dips into the emulsion, the latter is churned up and bubbles are formed, and the bearings become gummed up. *W* and *S* are the cold water and steam pipes, respectively.

To lead the emulsion into the trough the writer has been in the habit of using a very simple device which obviates the formation of bubbles and keeps the emulsion to temperature and is really very effective. A silver tube of one-sixteenth inch wall with three-eighths inch internal bore is provided at its center with a short two inch, T-piece, to which is attached the rubber hose leading from the emulsion stock pot. Each end of the tube is closed with a clean cork, and the whole length has a sixteenth inch slit cut in it. This pipe is placed in a muslin bag or loop, which is supported on two thin canes, the latter being long enough to rest on the ends of the trough, the muslin loop being just long enough to fit inside the trough. This arrangement is supported at the top of the coating trough close to *C* and the emulsion flows evenly and regularly down the slope towards *B*. It may be necessary just at first to induce it to flow in spots by leading it with the fingers, then the supply keeps up quite evenly.

The quantity of emulsion per unit area depends to a great extent on the nature of the same, and it is not difficult to determine with a few experiments exactly how much emulsion is picked up with a given speed of the celluloid. For on this, other things being equal, rests absolutely the quantity taken up. The faster the celluloid moves the more emulsion it will pick up and vice versa. There is one practice that the author has always followed, and that is to have fitted behind the front frame and pendent from the angle iron *GH*, a lantern fitted with a safelight screen, without paper between the glasses, and a 10 c. p. metal filament lamp. The front glass is blocked out with opaque paper, all but a strip two inches long across the front of the lantern. This was used to roughly gauge the thickness of the coating, and for positive work the thickness must be such that the shape of the filament is entirely lost; with negative emulsions as a rule, however, the filament should be just discernible. Naturally this is only a rough guide, but it is astonishing how expert a coater will become by experience in thus gauging the coating.

Fig. 32

The arms to carry the coating roller have the shape shown in Fig. 32, and the dimensions are as follows: The hole *A* is to fit a shaft one and eleven-sixteenths inches in diameter; the length from *B* to *C* is nine inches and the thickness of the metal five-eighths inch. Two ears project at *C*, three-quarters of an inch long, and a thumb screw runs through both so as to tighten the grip on the axle; a set screw *D* also being run through underneath to further prevent any slip. *E* is a quarter-inch screw with hard pointed end which engages in a socket in the end of the coating roller. This screw has a square head, so that it can be tightened with a pair of pliers. It may be noted that the trick of using such square-headed screws will be found much more practicable than the usual slotted head, as one need not grope about in the dim light for the slot. Two collars should be provided, one on each side of the arm on the axle, so as to keep it firmly in position.

The axle on which these arms work is fastened to a lever with toothed edge that engages with notches in a rack on an arc, with the handle moving in a slot, a small spring handle being provided to prevent any slipping from the notch. This enables one to lower the coating roller to any depth in the emulsion trough.

To thread up the machine a leader of unbleached calico, or preferably duck, should be fastened to the beginning of the celluloid. This leader must be long enough to pass up the front of the machine, over the suction box and to the first stick in the drying tunnel. A follower should also be fastened to the end of the celluloid in the same way, as this prevents the end of the celluloid dropping as it leaves the suction box. As this follower can be unfastened, it can be left on the machine to act as the leader for the next run. When the running is continuous, as it can be with sufficient length of drying tunnel and sufficient air supply, two or more lengths of celluloid may be joined up so as to make a very long run, but this means a rather unwieldy reel to handle.

To fasten the leader to the celluloid, one of the following schemes may be used. Thin hardwood strips may be used, about one-eighth inch thick and one inch wide, about half an inch longer than the celluloid. These can be folded in the ends of the cloth and celluloid as shown in Fig. 33, and clipped with hard brass spring clips, which must be long enough to pass completely over the folds. The method of folding the material and the celluloid is shown in detail; *D* is the cloth, *C* the celluloid, *WW* the sticks and *B* a spring clip. The surface *DC* is that which runs next to the machine and presents no obstacle to its travel over the suction box. Another plan is to provide two thin brass strips with holes punched through in pairs, and provide a sharp pointed lace which is threaded through eyelet holes in the material and through the celluloid. Yet another plan is to use strong metal clips with interlocking saw teeth, which are driven through both materials, the length of the clips being not less than two inches. They should be spaced, like the first-named clips, about every eight inches apart.

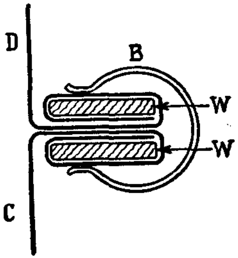

FIG. 33

Most things have a propensity to go wrong sometimes, and even the simplest machine will occasionally kick. It may be necessary, therefore, to get at the top of the suction box and for this purpose a narrow stairway should be built at one side of the machine; twelve inches is quite wide enough. The top of the machine should be entirely enclosed at the sides along the line of the upper bar *CI,* and a little doorway may be made for entrance. This is a good preventive of dust.

The celluloid is moved by the movement of the felt belt and this can be driven by the pulley *P* and can be connected by Morse or similar chain drive with a motor that can be easily housed directly under this end of the machine, where there is plenty of room. Instead of the chain drive, a direct connected shaft-drive with worm and gears may be used. The motor should be 10 H. P., with special reducing gear giving a drive speed of from 15 to 30 R. P. M. The regulation of the speed should be under manual control, with a push button starter located close to the coating trough, so that the operator may have full control over the motor. The motor must be fully enclosed and should comply with the specifications of the U. S. Government for motors of the explosion proof type. The drive must be perfectly regular without jerks, or these will show as rhythmic waves in the coating.

As soon as the celluloid leaves the pulley *P* it sags down, and the end must be caught and fastened to the first stick of the drying machine or a sufficient length pulled over so that the weight of the first loop does not cause it to slip; the former plan is preferable. The sticks are caught automatically by hooks on an endless chain and are carried along a trackway, and form the loops or festoons which travel down the length of the tunnel. Precisely the same arrangement is used for drying paper and has been adapted for film drying without change, and the hooks are arranged to give a loop measuring ten feet from the stick to the bottom of the loop, or in some cases even twenty feet. This, however, is a mistake for film, in the writer's opinion, and the hooks should be four feet six inches apart, which gives a shallow loop of only nine feet in total length, which is much less likely to cause curling and buckling of the celluloid.

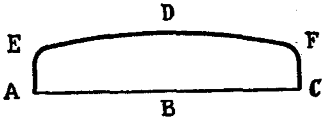

FIG. 34

The usual stick is practically a broomstick, but it has been found much better to give them the shape and dimensions shown in Fig. 34; *ABC* being three inches, *BD*, three-quarters of an inch and *AE*, *CF*, each one-half inch, with the upper corners slightly rounded off. This shape gives a much greater supporting surface for the film and is less likely to give stick markings. These pests become apparent as a marked curve in the celluloid, and with badly arranged drying control, frequently a thinner line due to the variation in rapidity of drying of the emulsion here.

The length of the drying tunnel will naturally depend upon the required output and the ground available. It is possible to arrange for the festooning chains to rotate round a turntable through 180 degrees, so that the dry film can be reeled close to the coating end; but if possible a straight run is preferable, with the reeler at the opposite end of the tunnel. The exact length of the tunnel will depend on the speed of the coating and rate of drying; but it has been found that with a speed of twenty-five feet per minute and suitable air supply, it is possible to work continuously with two hundred and fifty feet of tunnel.

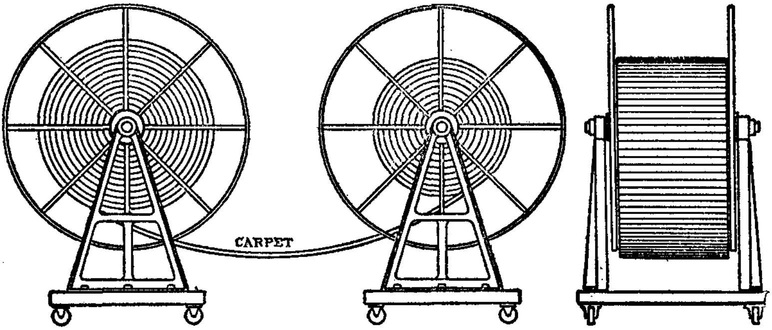

Fig. 35

In lieu of using the festooning arrangement, it is possible to use a reel with wooden-slatted carpet, as shown in Fig. 35. This naturally saves enormously in drying space, as a reel of about six feet diameter will easily take about two hundred and fifty feet of celluloid.[1] There is no chance for the celluloid to buckle or curl with this arrangement; but it is essential for some one to straddle the carpet and lead the celluloid between the ends of the slats, unless a perfect drive is obtained. The writer's experience with these reels has not been so happy as with the festooning. The main objection is that there is far more handling, as the reels have to be run into the drying rooms, and there is a greater chance of the wet emulsion picking up dust in its passage. On the other hand, for factories cramped for floor space, they are undoubtedly of great benefit. The difference in the rate of drying of the film is not much, provided the air supply is led directly through the spiral of the reel.

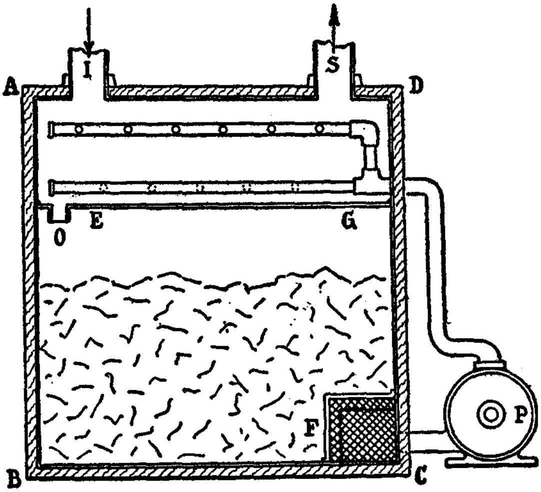

FIG. 36

The air used for drying must be washed with as cold water as possible, and must be again heated up to the required drying temperature.

A spray washer for small work may be made without very heavy expense on the following lines.

In Fig. 36, *ABCD* represents the longitudinal section of a stout galvanized iron tank, covered outside with insulating felt and with wood casing. *EG* is the floor of the spray chamber. Fig. 37 shows a cross section of the same, in which *ABCD* is the tank, *EG* the floor of the spray chamber, which as will be seen only occupies two-thirds of the top of the ice chest, of which *L* is the lid; *O* is an outlet pipe to carry off the water used for washing. *F* in Fig. 36 is a small chamber formed of coarse meshed wire cloth outside with a finer mesh layer inside, which acts as a filter. *P* is the pump, which forces the ice-cold water through the spray nozzles in the upper chamber. The ice chest must also be provided with an outlet with stopcock so as to reduce the water to the proper level.

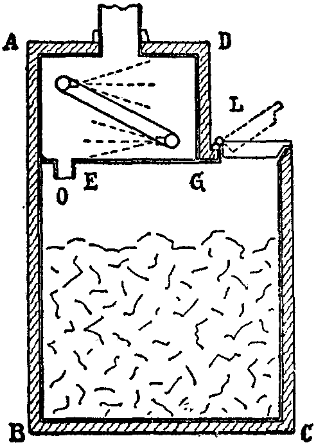

Fig. 37

The lower chamber should be about half filled with lump ice and the latter rammed down so as to get in as much as possible. The air is drawn in through *I* and sucked out through *S*. *I* should be connected to the drying room so that the air may be used over and over again.

A much simpler arrangement which can be adapted for only a dozen or two plates is to use a galvanized iron cylinder, as in Fig. 38. *ABCD* can be filled with lump ice, which should not be too small, so as to leave plenty of air space between the lumps. The air is sucked in at *I* and out at *O* and passes thence to the heating arrangement. *EF* is the floor on which the ice rests, and this can be stout perforated zinc, supported by iron bars. The water from the melting ice drops into the lower chamber *CD*, and runs away through an outlet pipe, which should be provided with a tap, so as not to allow unwashed air to be sucked through it.

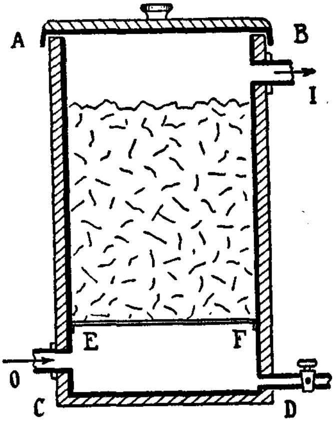

Fig. 38

The heating apparatus will naturally depend on the consumption of air, which is again dependent on the quantity of water to be dried out of the emulsion. With large consumption, steam heating coils will be used and the best arrangement for these is obviously in stagger formation, so that the washed air meets with as large a surface as possible. These pipes may be black japanned to protect them from the action of the moisture laden air; but it is necessary to run the steam for some little time to completely drive out the solvents. Galvanized iron piping can be used. For the smaller arrangements electric heating coils may be used, and two or three should be arranged in series so that two or more may be cut in or out to regulate the heat.

The colder the water for washing the air the better, and practically this may be considered to be about 2° C. (36° F.) under the above arrangements. The temperature of the washed air will then be about 4° C. (41° F.) and it should be heated up to about 40° C. (104° F.) before entering the drying tunnel. At the washing temperature, it has a relative humidity of approximately ninety per cent, but when heated to 40° C. this is reduced to about nine per cent, and the air is consequently very dry and very greedy of moisture. Probably the ideal system of drying, which is stated to have been used in one factory, is to wash the air with ice-cold water, then pass it over a refrigerating pipe system by which practically the whole of the moisture is frozen out, and then heat to about 15° C. (60° F.).

It is obvious that the smaller the actual drying tunnel, the better the utilization of the air is, for extra space round the film merely means that the air will for preference find its way round rather than over the film, naturally taking the path of least resistance. The ideal method of drying would be to force the air across the film loops, but this rather complicates the system of air ducts, for the air has naturally a tendency to escape with greater velocity near the blower than at fifty or one hundred feet from it. This means that the supply duct and the outlets must become narrower the further they are from the blower. The simpler plan is to force the air in at one end of the tunnel. This has one disadvantage and that is that the film has a tendency to become abnormally dry, with a consequent great tendency to curl and to the formation of static in reeling. It is far better to introduce the hot air at some distance from the tunnel end and allow the film to pass into a cold and relatively damp region so as to allow it to cool off and become slightly damper.

It may be useful to state that the longest length of motion picture film that is commercially available is four hundred feet and this is generally preferred to the two hundred feet lengths. These two are the standards, though it is possible to obtain one hundred feet lengths and even odd lengths; but for the usual camera and positive work the longer strips are preferred.

As regards the reeling of the film, this is a somewhat simple matter; the main point is to provide a friction clutch so as to compensate for the greater pull as the reel becomes larger, and to avoid as far as possible any contact with the coated surface. Evenness of the winding as regards the edges should be attended to and this can be effected to some extent by wooden guides. In no case must the ordinary paper reeling device be used, in which the paper passes in and out of a series of rollers.

There is one point in connection with the drying, which applies to all sensitive material, and that is the circulation of the air. It is claimed by some that it is sufficient merely to pump hot air into the room and allow it to find its way out; but as air always takes the line of least resistance, this may lead to dead-air pockets. A much more satisfactory plan is to provide also an exhaust fan at the opposite end to the intake, but of slightly less capacity than the blower, the result being that the room is always under a plenum, that is with an outward pressure, so that there is no tendency for unwashed air to suck in.

It will be found economical to return the air after its passage through the drying rooms to the washer, as it is obviously clean and merely requires cooling down. Usually by the time it returns the length of the tunnel it will be found cooled down to practically the temperature of the outer air. Some fresh air can always be mixed with it to keep the volume constant.

Thermometers and hygrometers should be installed at two or three points to enable one to check up the temperature and humidity; recording instruments are to be preferred, as the records can be sent to the office and be kept as a check on the engineer, and the author has known this to prevent disputes between the coating room and the engine room staff.

When the film is reeled it should be transported to the store room and it is as well to allow it to lie for a few days before use.

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[1] T. H. Blair, *Eng. Pat.* 5,504, 1893. An improved type of these reels can now be obtained from N. L. Scott & Co., London.

CHAPTER XII

DRYING

FOR experimental work and small batches as made by the amateur, the use of washed and heated air for drying is almost impossible, but there is not the slightest difficulty in using heated air. The writer's plan has already been outlined (see p. 167, where the use of a hairdressers' hot fan is described), and this will be found a great advantage and little trouble.

If electricity is not at command, a drying cupboard can be easily constructed without much cost, for use with gas. The main point in the use of gas is that the products of combustion should not have access to the plates; otherwise they will be hopelessly fogged.

The first cupboard is on the same principles as one laid down by England, one of the early experimenters and commercial plate makers. The objection to it is that the heat is too localized and the plates near the central pipe may melt. The objection to the Monckhoven type, in which a draught is created by a burning jet outside in a chimney, is that the air passing over the plates is not heated. This type of box may be satisfactory in very dry countries or on very dry days; but when the air is loaded with moisture, that is a humidity of 75 to 90, which is not uncommon, the time of drying is inordinately long and there is every chance of bacterial growth and spots. Much more satisfactory is Cowan's plan, in which the entering air is heated without the products of combustion entering the chamber.

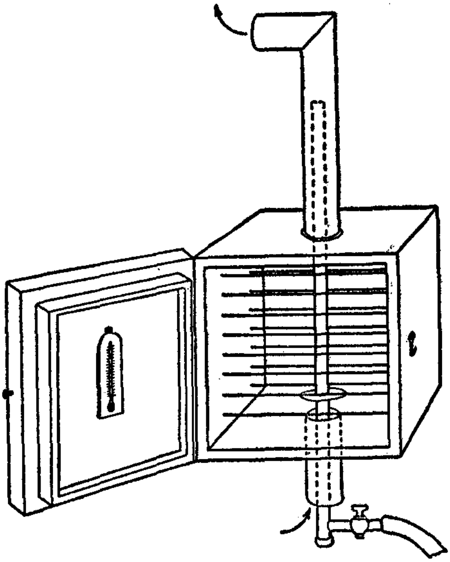

FIG. 39

There is, of course, a good deal of difference of opinion as to how high a temperature may be used in drying. Some contend that 30° C. (86° F.) is the highest permissible, others recommend much higher temperatures. Much depends upon the volume of air that is passed through the box, and its humidity. In the writer's experience, the drier the air and the more air used, the higher may be its temperature, and both plates and films have been successfully dried at 35° C. (95° F.). When panchromatizing motion picture film in the strip by bathing, it has been completely dried in twenty minutes at 38° to 40° C. (100° to 105° F.).

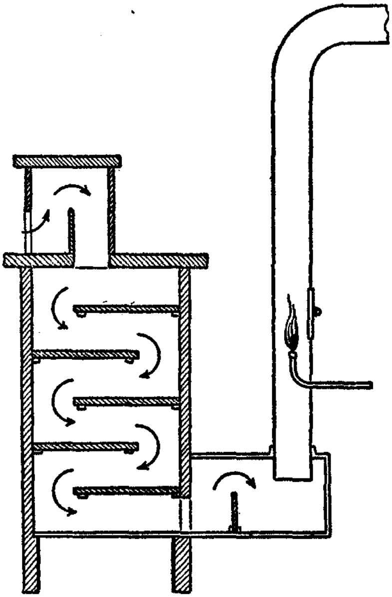

Fig. 40

England's drying cupboard is shown in Fig. 39. It is one by two by two feet, with stout iron wire shelves, and a central pipe carrying off the burnt gas passing through an outer pipe. The Monckhoven type is shown in Fig. 40. It will be seen that the shelves are solid and staggered, so that the air takes a zigzag course over the whole of the plates. The outlet pipe was originally connected with a chimney, which created the draught, but this is not sufficient to dry the plates rapidly and a gas jet, burning in a flue outside, is an improvement.

Cowan's box, Fig. 41, is the best, as there is no chance of the burnt gas gaining access to the plates, and the air can be thoroughly heated. One good feature of this is the sliding door, an improvement on those which open on hinges, as it is out of the way. This box can be improved by fitting a small exhaust fan in a pipe at the top, as then the circulation of the air is much greater and one need not be so careful as to temperature.

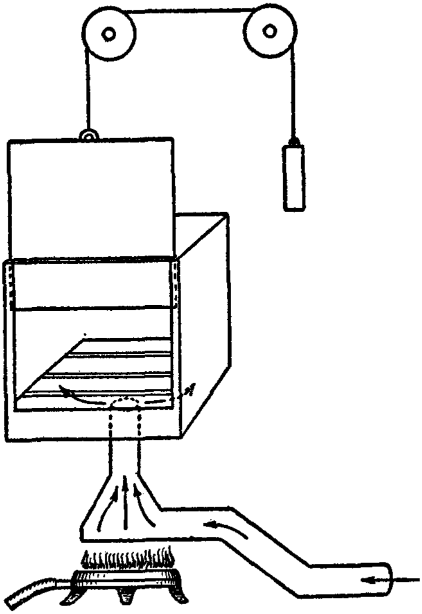

Fig. 41

In commercial establishments, the air is thoroughly washed by being sucked through one or more water sprays, the water being chilled as much as possible. This washes out all dirt and dust, from which it is unusual to find air wholly free. At the same time the air becomes saturated with moisture and is then passed over a heating system, usually staggered coils of steam pipes, by which it is raised to the desired temperature, thence blown into the drying room or cupboards. By thus heating the air, which may be raised from a temperature of about 5° C. (41° F.) to 35° C. (95° F.), it naturally becomes very dry and is then extremely greedy of moisture, so that the plates dry very quickly.

The expense of an efficient air-washing and heating apparatus is fairly heavy. To avoid this some have used Canton flannel or fine canvas soaked in a hygroscopic liquid, such as glycerine, sugar syrup or even heavy oil, through which the air is sucked. This plan is not to be recommended, as the fabric soon becomes so loaded with dirt that the interstices are clogged and the air supply is cut down. Besides, the cloth wants washing every two or three days.

For experimental work it will be found that the electric heaters are far more convenient than gas, and provided that they are not varnished with black varnish, they will not affect the emulsion. If varnished they should be run till this ceases to give any smell, as these vapors have a tendency to fog.

It is usual to stack the coated plates in racks, which are generally made for the purpose. The ordinary small rack, as made for negative drying, is the least suitable of any, for the plates are too close together and the grooves too deep, so that if used they would stick to the sides of the wet plates. A suitable form of rack is shown in Fig. 42. The base may be merely a frame of hard wood, about one inch thick. Into the upper surface of this should be let short upright wooden rods; these need not be more than four inches in height and about one-half inch in diameter. They should be spaced not less than one and a half inches apart. Provided there is plenty of drying space at command, the distance between the upright rods may be increased to two or three inches, thus giving greater freedom for the air to travel between. The base plate or frame should be flat underneath, without any projections, which are liable to catch on the shelves.

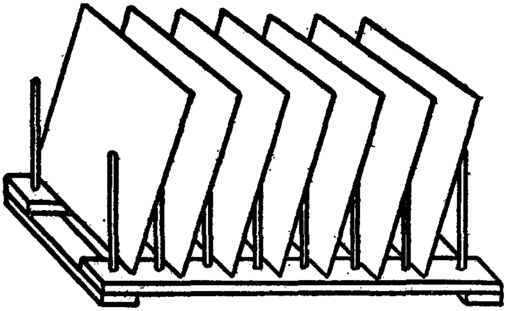

Fig. 42

In some factories the racks are merely stacked on shelves and the warm air pumped in at one end and sucked out at the other. In this case, as already pointed out, the capacity of the exhaust fan should be rather less than that of the intake so as to form a plenum in the room. Far preferable to this plan, which may lead to irregular and longer drying in consequence of the hot air taking the lines of least resistance, is to build cupboards or tunnels, wide enough to take one or two racks side by side. These tunnels should be entirely enclosed, with an inlet for the hot air at the bottom at one end and an outlet at the other end at the top. Sliding doors may be fitted in one of the longer sides, giving access to the shelves. The most elaborate system of this kind had doors at one end and was provided with endless bands of narrow duck, working over rollers at each end. The operator had merely to turn a wheel at the side of the tunnel to run any rack, placed on the bands, to the far end of the tunnel. Several such bands were placed one above the other in the height of the tunnel, the space between being designed for the size of the plates. At intervals along the length of the tunnels rollers were placed, which facilitated the running of the bands and prevented them from sagging too much under the weight of the racks. There being no solid shelves, there was no serious obstruction to the passage of the air.

The length of time taken in drying will, as already pointed out, depend on the volume of air and its temperature, and also on the number of plates stacked in the room or tunnel. In the early days eight to ten hours was considered the normal time of drying, but with improved arrangements this has been cut to three or four hours. It is extremely important that the emulsion should dry evenly, otherwise zones of irregular density will become apparent on development.

The main point in all drying systems is that there should be as rapid a change of air as possible. This is more important than greater heat. If this be effected, the plates will stand a heat greater than that required to actually melt the emulsion, because the change of air carries off the evaporated water, whereas if the air is stagnant it becomes saturated with moisture and then there is no chance for the water, held by the gelatine, to escape, and everyone knows that the more water a gelatine contains, the lower the melting point.

For small experimental batches the simplest drying box is a metal box, such as the ordinary metal deed case. The edges should be provided with strips of draught-excluding rubber so as to make them airtight, when the box is closed. In the center of the box should be placed a block of wood of such a height as to allow of a dish being placed thereon without interfering with the closure of the case. In this dish should be placed some anhydrous calcium chloride; this need not be pure, merely that obtainable commercially for drying purposes. It should not be in too large lumps, about the size of a walnut is the best, as they present a sufficiently large area to the air and yet allow free access round them. Sheets of blotting paper may be placed on the bottom of the box to prevent the plates from slipping on the metal. Provided such an arrangement is placed in a normally warm room, and too many plates are not put in it at once, the drying goes on quite satisfactorily and reasonably quickly, without any trouble. It is possible also to dry experimental plates by immersing in successive baths of alcohol, but this will obviously not give one so sure a guide as drying by air, as commercially this could not be done.

In one instance a somewhat peculiar method has been met with. As has been pointed out, it is usual to wash the air and in the case in question ammoniacal water was used, so that the drying chambers were always charged with ammonia vapor, which obviously must have had some influence on the film. From comparative experiments, however, the increase in speed found by this method by the writer did not warrant adoption of the process, as it did not amount to ten per cent of that obtained with plates of the same emulsion dried in the usual way.

CHAPTER XIII

Appendix

The formulas collected here may present some features of interest, and in all cases the author and reference are given, except in those cases in which the formulas have been given to the writer as being used commercially, in which case they are merely designated by X. No attempt has been made to give all the methods that have been gleaned from various sources, particularly the early ones which are obviously now out of date.

Negative Emulsions. —
Fast-acid process (Eder, *Handbuch,* **3**, 371):

Potassium bromide	625 to 750 g
Potassium iodide	12.5 g
Hard gelatine	250 g
Water	2500 ccm

Temperature 60° C. (140° F.). Add:

Silver nitrate	500 g
Water	1750 ccm

Temperature 20° C. (68° F.). Boil for forty-five minutes and add:

Gelatine	250 g
Water	2000 ccm

Set and wash. Increase of speed and density can be obtained as with all boiled emulsions by cooling down to 35° C. (95° F.) before adding the last gelatine, and adding:

Ammonia	37.5 to 125 ccm

Then digest for thirty minutes at 35° to 40° C. (95° to 104° F.), then add the last lot of gelatine and set.

Slow-acid process (Eder, *Handbuch*, 3, 371):

Ammonium bromide	335 g
Potassium iodide	10 g
Gelatine	335 g
Hydrochloric acid 1:3	1 to 3.5 ccm
Water	3330 ccm

Temperature 60° C. (140° F.) Add:

Silver nitrate	500 g
Water	2075 ccm

Temperature 20° C. (68° F.). Boil fifteen to thirty minutes, then add:

Gelatine	335 g
Water	3330 ccm

Temperature 30° to 40° C. (86° to 104° F.). Set.

Fast-ammonia process (Eder, *Handbuch*, 3, 368):

Ammonium bromide	665 g
Potassium iodide	11.3 g
Gelatine	200 g
Water	4150 ccm

Temperature 60° C. (140° F.). Add:

Silver nitrate	500 g
Water	4150 ccm
Ammonia	q. s.

Temperature 20° C. (68° F.). Digest forty-five minutes at 40° C. (104° F.). Set.

Fast (Plener, *Handbuch*, 3, 367):

In this process as low a temperature as possible is used, but it is a little difficult to carry out on a large scale. Four solutions are required:

I.	Silver nitrate	500 g
	Water	2500 ccm
	Ammonia	q. s.

Temperature 20° C. (68° F.).

II.	Ammonium bromide	400 g
	Potassium iodide	10 to 15 g
	Water	2500 ccm

Temperature 20° C. (68° F.).

III.	Hard gelatine	400 g

This should be allowed to soak in water from one to two hours, the excess of water drained off and the gelatine melted at 35° to 45° C. (95° to 113° F.).

IV.	Hard gelatine	250 g

Allow to swell in water, pour off excess and melt, and add just before using:

Ammonia	250 ccm

A tall narrow flask should be used, so that, in shaking, as much froth as possible is formed. To solution II add one-tenth of III. Shake well till the flask is filled with froth; the colder the solutions the less gelatine required. Then the silver solution

I should be sprayed in with constant shaking. As soon as all the silver has been added, immerse the flask in a water bath at 35° C. (95° F.) for a few minutes and add the remainder of III, warmed to 35° to 45° C. (95° to 113° F.) with frequent shaking, and digest for thirty minutes at 35° to 45° C. (95° to 113° F.). Then add IV and digest another fifteen minutes. Pour out into a flat dish to the depth of two to three centimeters, cover with a card and allow to stand one or several days, up to six days, a test being taken every day. The best temperature for the cold digestion is 10° to 15° C. (50° to 59° F.). This method gives rapid emulsions with high gamma infinity, and the colder the solutions during the mix the less the fog.

Fast-ammonium carbonate process (X):

Potassium bromide	400	g
Potassium iodide	20	g
Soft gelatine	50	g
Water	2900	ccm

Temperature 50° C. (122° F.). Add:

Silver nitrate	500	g
Nitric acid	1	ccm
Water	1465	ccm

Temperature 50° C. (122° F.). Then add to the emulsion:

Ammonium carbonate	40	g
Water	290	ccm

Time of mixing, four minutes. Gradually raise the temperature to 90° to 93° C. (194° to 199° F.).

Then cool in thirty minutes to 55° C. (131° F.) and add:

Hard gelatine, dry	400 g

Stir thirty minutes and set. Wash eight hours and drain two to four hours. Melt to 50° C. (122° F.) and make up to 9330 g, filter and set. After six hours, remelt to 43° C. (110° F.) and add:

Hard gelatine, dry	300 g

Make up to 11,665 g.

Fast (G. T. Harris, *Amer. Ann. Phot.,* 1916):

Soft gelatine	10 g
Potassium iodide	15 g
Water	310 ccm

Temperature 71° C. (160° F.). Add:

Silver nitrate	15 g
Water	310 ccm

Temperature 71° C. (160° F.). Then add to:

Potassium bromide	400 g
Soft gelatine	75 g
Hydrochloric acid, 10% sol.	22.5 ccm
Water	2500 ccm

Temperature 71° C. (160° F.). Then add:

Soft gelatine	65 g
Water	1250 ccm

Temperature 71° C. (160° F.). Add to:

Silver nitrate	485 g
Water	1575 ccm

Digest for forty minutes or till blue by transmitted light, then lower the temperature and digest for twenty minutes till grey, and add:

Ammonia, 10% sol.	250 ccm
Gelatine	270 g

Digest for two and a half hours at 20° C. (68° F.) and add:

Gelatine	270 g

Set and wash. This is said to give a speed of 225 H. & D.

Fast-ammonia process (X):

Ammonium bromide	348 g
Potassium iodide	5.5 g
Gelatine	93 g
Citric acid	3.25 g
Water	1850 ccm

Temperature 55° C. (122° F.). Add:

Silver nitrate	500 g
Water	925 ccm
Ammonia	q. s.

Temperature 20° C. (68° F.). Allow to stand fifteen minutes and add:

Gelatine	370 g

Allow to stand forty-five minutes and set. Wash forty minutes, melt to 50° C. (122° F.) and add:

Gelatine	460 g

Cool to 32° C. (90° F.) and add:

Ammonia	45 ccm

Digest twenty hours and add:

Ammonia	22.5 ccm

Digest another twenty hours and add:

Ammonia	22.5 ccm

Digest another twenty hours. Set and wash, and add:

Alcohol	460 ccm

When tested this gave fast but foggy results, with low gamma infinity.

Fast-acid process (G. T. Harris, *Brit. J. Almanac,* 1896, 705):

Potassium bromide	414 g
Barium iodide	16.8 g
Gelatine	70 g
Hydrochloric acid, 1 : 3	10 ccm
Water	3250 ccm

Temperature 60° C. (140° F.). Add, immediately before emulsification:

Erythrosin, 1% sol.	53 ccm

Then add:

Silver nitrate	500 g
Water	3250 ccm

Temperature 60° C. (140° F.). Boil for forty-five to sixty minutes and add:

Hard gelatine	650 g

Set and wash thoroughly, and add:

Chrome alum	5 g
Water	250 ccm

and:

Phenol	5 g
Alcohol	250 ccm

There may be some particular virtue in the use of the barium iodide which is not apparent, but 12 g potassium iodide may be used instead. Although the quantity of acid in the bromized gelatine is small, it would decompose some of the erythrosin.

Fast-ammonia process (X):

Potassium bromide	380 g
Ammonia	100 ccm
Gelatine	50 g
Water	1750 ccm

Temperature 45° C. (113° F.), then cool to 35° C. (95° F.) and add:

Silver nitrate	125 g
Water	750 ccm
Ammonia	q. s.

Temperature 18° C. (65° F.). Raise to 38° C. (100° F.) slowly and add:

Potassium iodide	20 g
Water	200 ccm

Temperature 18° C. (65° F.). Then add:

Silver nitrate	375 g
Water	1500 ccm

Temperature 18° C. (65° F.). Raise to 44° C. (111° F.) and add:

Gelatine, dry	200 g

Then cool to 32° C. (90° F.) and digest for twelve hours. Set for sixteen hours, then melt to 38° C. (100° F.), and add:

Gelatine, dry	700 g

As soon as dissolved, cool down and set. Wash next day for two to four hours with water not higher than 15° C. (59° F.) and drain four hours. Melt and add:

Alcohol	750	ccm
Hydrobromic acid, 10% sol.	37.5	ccm
Thymol, 5% alc. sol.	50	ccm
Glycerine	75	ccm

Medium (Eder, *Handbuch,* 3, 365):

Ammonium bromide	335 to 500	g
Potassium iodide	5	g
Hard gelatine	665	g
Water	4150	ccm

Temperature 40° to 60° C. (104° to 140° F.). Add:

Silver nitrate	250	g
Water	2075	ccm
Ammonia		q. s.

Temperature 20° C. (68° F.). Add:

Silver nitrate	250	g
Water	2075	ccm

Temperature 20° C. (68° F.). Digest forty-five minutes, set and wash:

Or:

Ammonium bromide	335	g
Potassium iodide	5	g
Gelatine	666	g
Ammonia	166	ccm
Water	4165	ccm

Temperature 40° C. (104° F.). Add:

Silver nitrate	500	g
Water	4165	ccm

Temperature 20° C. (68° F.). Digest forty-five minutes and set.

Slow-ammonia process. (Eder, *Handbuch,* **3**, 363):

The same formula as above may be used and digested for thirty-five to forty minutes at 35° C. (95° F.), and poured into a flat dish to the height of two to four centimeters.

Fast-ammonia process (Cobenzl, *Jahrbuch,* 1919, **23**, 119):

Potassium bromide	359	g
Potassium iodide	8.3	g
Ammonium chloride	17	g
Gelatine	780	g
Water	6666	ccm

Temperature 45° C. (113° F.). Add drop by drop at first, and then faster:

Silver nitrate	250	g
Water	550	ccm
Ammonia		q. s.

Then add:

Silver nitrate	250	g
Water	650	ccm

Digest for forty-five minutes at 45° C. (113° F.), set and wash, and add:

Gelatine, swollen	234	g

Make bulk to 17,000 g. Cobenzl states that the presence of some silver chloride gives more delicate gradation, but as a matter of fact no chloride is formed, as there is enough iodide and bromide to completely convert the silver.

Transparency (Bohrer, *Jahrbuch,* 1899, **13**, 188):

Potassium bromide	400 g
Potassium iodide	20 g
Ammonium carbonate	125 g
Gelatine	165 g
Water	4500 ccm

Temperature 70° C. (158° F.). Add:

Silver nitrate	500 g
Water	1565 ccm

Temperature 70° C. (158° F.). Digest for two hours at 90° C. (194° F.) and add:

Gelatine	500 g

This should be previously soaked for one hour. Set and wash. For matt emulsions, add 30 to 40 g rice starch per liter. This reads almost like a bromide paper formula.

Bromide Paper Emulsions. —

Mix:

Ammonium bromide	300 g
Potassium iodide	33 g
Gelatine	833 to 1333 g
Water	6665 ccm

Temperature 50° to 60° C. (122° to 140° F.). Add:

Silver nitrate	500 g
Water	6665 ccm

Digest fifteen to sixty minutes and set. This gives dark brown tones. The addition of:

Citric acid	333 g

to the bromized gelatine, gives warmer browns. If the acid is omitted and after mixing:

Ammonia	66 ccm

be added, darker browns are obtained. For pure black tones omit the iodide and increase the bromide to 333 g (Eder, *Handbuch,* **3,** 363).

For black tones:

Potassium bromide	402 g
Gelatine	670 g
Nitric acid	0.5 ccm
Water	6700 ccm

Temperature 30° C. (86° F.). Add:

Silver nitrate	500 g
Water	6700 ccm

Temperature 30° C. (86° F.). Digest forty-five to sixty minutes, set and wash. For brown tones, use 335 g of potassium bromide and 71.4 g potassium iodide, the other ingredients and method of mixing as above (Hallenbeck, *Amer. Ann. Phot.,* 1897, 342).

Mix:

Ammonium bromide	375 g
Gelatine	500 g
Water	5000 ccm

Temperature 50° C. (122° F.). Add:

Silver nitrate	500 g
Water	5000 ccm

Temperature 50° C. (122° F.). Digest for one hour at 66° C. (150° F.). Set. (R. Child Bayley, *Photogram,* 1896, 84).

Mix:

Potassium bromide	393 g
Citric acid	9.3 g
Chrome alum	13 g
Gelatine	857 g
Water	17140 ccm

Boil for seven minutes and add:

Silver nitrate, dry	500 g

Stir for twenty minutes and set, wash and melt and add:

Alcohol	1785 ccm

Make the bulk to 21,430 ccm. (Haffel, *Phot. News,* 1891; *Jahrbuch,* 1892, 6, 384).

Dissolve:

Gelatine	332 g
Water	1685 ccm

Temperature 50° C. (122° F.). Add:

Potassium bromide	462 g

Citric acid	462 g
Water	1685 ccm

Temperature 50° C. (122° F.). Cool to 38° C. (100° F.). Add:

Silver nitrate	500 g
Water	2500 ccm
Ammonia	q. s.

Temperature 18° C. (65° F.). Digest at 38° C. (100° F.) for forty-five minutes and add:

Gelatine	332 g
Water	1685 ccm

Set and wash, melt to 43° C. (110° F.). Add:

Gelatine	332 g
Water	1685 ccm

with the usual additions (X).

Mix:

Gelatine	1110 g
Zinc chloride	389 g
Cadmium chloride	1.85 g
Cadmium iodide	1.85 g
Water	12000 ccm

Dissolve at 70° C. (158° F.). Add:

Alcohol	4630 ccm

Then add:

Silver nitrate	500 g
Water	1850 ccm
Alcohol	925 ccm

Digest at 80° to 90° C. (176° to 194° F.) for one and a half hours and rapidly cool down with constant stirring. At about 15° C. (68° F.), the silver bromide settles out as a granular powder, which should be separated from the supernatant liquid, and after a brief wash, should be added to:

Sodium carbonate	1.85 g
Ammonium bromide	1.85 g
Gelatine	1110 g
Water	22222 ccm

Temperature 35° C. (95° F.). When thoroughly emulsified, add:

Chrome alum, basic 10% sol.	37 ccm

This is stated to give a very vigorous and clean-working emulsion. Presumably the gelatine will remain in solution in the first mixture, but it is a very large quantity in face of the alcohol content. Obviously the use of the metallic halides is a throw-back to the wet collodion days. The basis of the method is Henderson's process, see p. 241. (Cobenzl, *Jahrbuch,* 1909, **23,** 119).

Mix:

Potassium bromide	360 g
Ammonium chloride	16.5 g
Potassium iodide	8.25 g
Hard gelatine	780 g
Hydrochloric acid	0.5 ccm
Water	6650 ccm

Temperature 45° C. (113° F.). Add at first drop by drop, and then faster:

Silver nitrate	250 g

Water	550 ccm
Ammonia	q. s.

Then add:

Silver nitrate	250 g
Water	650 ccm

Digest twenty-five minutes at 45°C. (113° F.). Pour out into a flat dish. After washing, melt and add:

Hard gelatine	235 g

This should have been previously swollen in water. When dissolved, add:

Chrome alum, basic, 10% sol.	35 ccm
Water to	17000 ccm

(Cobenzl, *ibid.*)

Mix:

Potassium bromide	687 g
Potassium iodide	12.5 g
Potassium chloride	2.5 g
Hard gelatine	250 g
Water	2500 ccm

Temperature 60° C. (140° F.). Add:

Silver nitrate	500 g
Water	1875 ccm

Temperature 60° C. (140° F.). Then add:

Medium gelatine	250 g
Water	2500 ccm

Set.

Or:

Ammonium bromide	333 g

Hard gelatine	333	g
Potassium iodide	10	g
Water	3330	ccm

Temperature 60° C. (140° F.). Add:

Silver nitrate	500	g
Water	2500	ccm

Then add:

Gelatine	330	g
Water	2500	ccm

Digest for fifteen to sixty minutes at 70° C. (158° F.). After washing, add:

Chrome alum, sat. sol.	50	ccm

For matt emulsions, add:

Rice starch	165	g
Water	330	ccm

(K., *Der Phot.,* 1922, 93).

DEVELOPMENT (GASLIGHT) PAPER EMULSION. — Mix:

Potassium bromide	50	g
Ammonium chloride	300	g
Hydrochloric acid	0.5	ccm
Hard gelatine	1000	g
Water	10000	ccm

Temperature 40° C. (104° F.). Add:

Silver nitrate	60	g
Water	200	ccm
Ammonia		q. s.

Temperature 18° C. (68° F.). Then add:

Silver nitrate	440	g
Water	2000	ccm

Temperature 18° C. (68° F.). Set at once and add after washing:

Gelatine, swollen	200	g
Chrome alum, basic 10% sol.	50	ccm
Water to	20000	ccm

(Cobenzl, *Jahrbuch,* 1911, **25**, 119)

PRINTING-OUT PAPER EMULSIONS. —

Melt:

Gelatine	260	g
Water	1200	ccm

Temperature 50° C. (122° F.). Add:

Citric acid	40	g
Ammonium chloride	10	g
Rochelle salts	10	g
Water	600	ccm

Temperature 50° C. (122° F.). Add:

Silver nitrate	100	g
Water	300	ccm

Temperature 18° C. (65° F.) Digest for one hour at 50° C. (122° F.) and add:

Alcohol	120	ccm

(X).

Take:

Gelatine	400	g
Water	4000	ccm

Soak for two hours, melt to 55° C. (131° F.) and add:

Citric acid	70 g
Ammonium chloride	12.5 g
Rochelle salts	12.5 g
Water	250 ccm

Then add:

Alcohol	150 ccm
Chrome alum	1.25 g

(X).

Mix:

Medium gelatine	250 g
Sodium chloride, c. p.	21 g
Water	2500 ccm

Temperature 40° C. (104° F.). Add:

Citric acid	30 g
Tartaric acid	10 g
Water	450 ccm

Temperature 40° C. (104° F.). Add:

Ammonia, 10% sol.	40 ccm

Digest from thirty to sixty minutes and add:

Chrome alum, basic 10% sol.	10 ccm
Water to	3800 ccm

(Cobenzl, *Jahrbuch,* 1911, **25**, 119)

Casein P.O.P.—

Take:

Casein	500 g
Caustic soda	10 g
Water	1000 ccm

Heat till dissolved and allow to stand twenty-four hours. Filter and add:

Glacial acetic acid	q. s.

to precipitate the casein, wash till free from acid, rinse with alcohol, and then with ether, dry and powder.

Alcohol	1300 ccm
Casein, made as above	100 g

Heat to 38° C. (100° F.) and add:

Glacial acetic acid	90 ccm
Calcium chloride, anhydrous	12.5 g

Dissolve and add:

Alcohol	100 ccm
Citric acid	25 g

Then add:

Camphor	30 g
Alcohol	100 ccm

Then add the following at 38° C. (100° F.):

Silver nitrate	100 g
Glycerine	30 ccm
Alcohol	100 ccm
Water	300 ccm

Dry the paper at 38° to 44° C. (100° to 110° F.) (X).

SELF-TONING GELATINE PAPER. —

Mix:

Ammonium chloride	13 g
Citric acid	52 g

Aluminum nitrate	4.5 g
Alum	9 g
Gelatine	500 g
Water	4000 ccm

Temperature 52° C. (126° F.). Add slowly:

Gold chloride	4.5 g
Alcohol	700 ccm

Then add:

Ammonia	20 ccm

Heat the mixture to 43° C. (110° F.) and add:

Silver nitrate	100 g
Water	920 ccm

Make bulk to 6,100 ccm and allow to stand one hour before coating (X).

Melt:

Hard gelatine	185 g
Water	1540 ccm

Temperature 45° C. (113° F.). Filter and add:

Citric acid	20 g
Ammonium citrate	20 g
Rochelle salts	12 g
Lithium chloride, anhydrous	5.5 g
Water	415 ccm

Then add:

Potassium-gold chloride	4.5 g
Water	230 ccm
Gelatine	92.5 g
Water	769 ccm

Temperature 45° C. (113° F.). Add:

Silver nitrate	100 g
Water	287 ccm

Coating temperature 37° to 40° C. (99° to 104° F.). The above quantity should coat 38 meters of paper 66 cm wide (X).

Backing. —

Black, for panchromatic plates:

Yellow dextrin	80 g
Water	85 ccm

Heat till dissolved and mix in:

Ivory sienna black	900 g
Phenol	15 g

The ivory sienna black is obtainable commercially as a paste ground in water.

Red, for ortho and ordinary plates:

Use the same formula, but with burnt sienna ground in water.

Some commercial plates are backed with a thin layer containing desensitizing dyes, which diffuse into the developer, thus exerting their peculiar action. It is obvious that any of the desensitizing dyes may be used in this way.

Henderson's Process. —

A. L. Henderson recommended a method in which the gelatine emulsion is precipitated by alcohol, a modification of Wratten's early precipitation method. Henderson's idea was to obviate the decomposition of the gelatine by the acid boiling or ammonia digestion, and for a time his process had many adherents, but the uncertainty of the results, due to the non-control of the temperature, led to its disrepute. On the other hand T. Bolas[1] stated: "As far as I know, there is nothing of fundamental importance in emulsion matters that was not published in the early eighties, although certain important matters then published have only been recently generally realized during the past few years, as for example the importance of precipitation by alcohol and maturation in alcohol as a means for avoiding deterioration of the gelatine, together with a realization of the highest sensitiveness. . . . For alcoholic ripening or maturation the purest alcohol is essential if constant results, certain results and the best results are to be obtained." Eder stated that the alcohol may be replaced by acetone.

Henderson gave several modifications of his process, and these are dealt with chronologically. The first was described as a "hot weather emulsion": [2]

Hard gelatine	547	g
Ammonium bromide	375	g
Ammonia	139	ccm
Water	2192	ccm
Alcohol	2192	ccm

Temperature 49° C. (120° F.). Add:

Silver nitrate	150	g

Water	822 ccm
Alcohol	822 ccm

Temperature 49° C. (120° F.). Add:

Silver nitrate	350 g
Water	1096 ccm
Alcohol	1096 ccm

Temperature 49° C. (120°F.). Allow to stand for a few minutes and add:

Alcohol	8768 ccm

keeping the emulsion warm, and stirring well all the time. The precipitated emulsion adheres partly to the stirring rod and partly to the bottom of the jar. Pour off the alcohol and allow the emulsion to cool, shred and wash in several changes of cold water and make the bulk to 13,580 ccm.

A modification of the above was given later:[3]

Gelatine	32 g
Water	1096 ccm

Add, mixed together:

Ammonia	548 ccm
Alcohol	2740 ccm

Then add in a fine stream:

Silver nitrate	500 g
Water	2740 ccm

Then add:

Gelatine, dry	900 g

As soon as the gelatine is all melted, the emulsion being kept at the above temperature, which should be that of all the solutions, add slowly with constant stirring:

Alcohol	13150 ccm

warmed to 32° C. (90° F.). The emulsion remains suspended in a flocculent state in the liquid. The jar should be placed in cold water and in a short time the emulsion settles down to the bottom as a cake and the liquid may be poured off, the emulsion broken up and washed, melted and the bulk made up to 8770 or 11000 ccm.

Another modification was also given,[4] which was essentially a cold emulsification process, and which is usually designated as Henderson's process:

Gelatine	25 g
Water	1096 ccm

Dissolve and add:

Ammonium carbonate	50 g
Potassium bromide	375 g
Potassium iodide	5 g

Then add, mixed together:

Alcohol	3288 ccm
Ammonia	137 ccm

Allow the mixture to get quite cold and add:

Silver nitrate	500 g
Water	2192 ccm

Allow to stand one hour with occasional stirring, and add:

Gelatine	750 g

Warm till dissolved and add:

Alcohol	13150 ccm

warmed to 32° C. (90° F.). When cold the emulsion will be at the bottom of the jar and should be shredded and washed and made up to 8,770 or 11,000 ccm. It will be noted that this differs from the previous one only in the use of ammonium carbonate instead of ammonia.

Henderson was a most enthusiastic emulsion experimenter and he evolved another formula:[5]

Potassium bromide	375 g
Gelatine	10.5 g
Water	468 ccm

Dissolve and add:

Alcohol to	4680 ccm

Then add:

Silver nitrate	250 g
Water	250 ccm
Alcohol	2340 ccm
Ammonia	q. s.

Enough ammonia should be used to form a clear solution. Then add:

Silver nitrate	250 g
Water	250 ccm
Alcohol	2340 ccm

Place in a water bath at 49° C. (120° F.) and add:

Gelatine, dry	500 g

When dissolved allow to cool, set and wash as usual.

Various modifications of Henderson's method were suggested but the following only seems worth record, and was given by Sresniewski:

Potassium bromide	400 g
Potassium iodide	10 g
Soft gelatine	50 g
Ammonium carbonate	50 g
Water	1000 ccm

Temperature 20° C. (68° F.). Add:

Silver nitrate	500 g
Water	2000 ccm
Nitric acid	1.25 ccm

Then add the emulsion slowly with continual stirring to:

Alcohol, 95%	2500 ccm
Ammonia	200 ccm

Temperature 20° C. (68° F.). Keep the emulsion at room temperature for eight to ten hours and add a warm solution of:

Gelatine	900 g
Water	6000 ccm

Precipitate with alcohol or set and wash with water.

Abney[6] stated that the following method, suggested by A. Cowan, had not been published and that it gave him the greatest rapidity he had obtained:

Ammonium bromide	350 g
Water	1500 ccm
Soft gelatine	75 g

The gelatine should be first washed with water to remove the dust and the washing water immediately poured off. Dissolve the gelatine and cool down and add in a fine stream to:

Silver nitrate	500	g
Water	600	ccm

previously mixed with enough ammonia, diluted with an equal volume of water, to form a clear solution. Then add with constant stirring:

Potassium iodide	25	g
Water	150	ccm

Then add:

Gelatine	400	g
Water	1800	ccm

dissolved and cooled to 28° C. (82° F.). Mix well and pour out to set. If kept for a day this gives a very fast emulsion. After washing and draining add:

Alcohol	750	ccm

If the emulsion is too thin add:

Hard gelatine	100	g

All the solutions should be cold when mixed. It will be seen that the essence of all these methods is the formation of the silver halides in the presence of a very small quantity of gelatine.

BARYTA PAPER. — Baryta paper is frequently used as the support for emulsions both for printing-out and development. It was first used for the former kinds, probably with the idea of insulating the sensitive emulsion from the raw stock so as to prevent as far as possible the wandering of the free silver into the paper fibers, with consequent decomposition of the salt and staining of the paper. With the more general use of bromide paper the same support was used to obtain particular surfaces, either the highly glazed, the matt or half-matt.

This paper is coated with an insoluble emulsion of barium sulphate, otherwise known as "barytes," "blanc-fixe," "permanent white," etc.

To undertake the preparation of this on a small scale cannot be advised. It entails a special coating machine, with which the baryta emulsion is evened out by reciprocating brushes; three or more coatings one on top of the other; and then calendering, that is, passing it four or six times through a series of five or seven heavy steel rollers with a pressure of thousands of pounds, after the surface has been moistened in another special machine.

On the other hand a thin baryta coating is sometimes given to a paper to impart a special surface, generally half-matt. This can be done on the ordinary coating machine and the calendering omitted.

The most practical description of the preparation of the baryta emulsion has been given by T. Bentzen and the following is a resumé: It is essential that the coating be evenly applied without lumps or waves and have the desired surface. It must be sufficiently hardened so that the warm silver emulsion cannot soften and penetrate it. At the same time it must be supple and not brittle when dry.

It is advisable to use distilled water only. Hard and medium gelatines should be used and mixed 2 : 1, 1 : 1, or 1 : 2, according to the time of year, the harder being used in summer. A ten per cent solution of the gelatine should not melt below 32° to 34° C. (90° to 93° F.). The setting point should not be below 22° to 26° C. (72° to 79° F.). It is always advisable to mix two or three different batches of gelatine and not rely on one only, as greater regularity is thus obtained.

The baryta is obtainable as a fine white dry powder, that is only used for dead-matt surfaces, also in paste form containing from twenty to twenty-five per cent of water, for half-matt and glossy surfaces.

It is necessary in these last two cases to determine the quantity of water they contain, as the ratio for the actual baryta coat is based on the dry baryta and not on the paste. This determination can, of course, be done in the usual way, that is by taking a known weight, as 100 g, drying in an oven to a constant weight and reweighing. The difference between the initial and the final weights obviously represents the quantity of water the paste contains.

If the baryta coating is to be tinted, the color must be so intimately mixed that streaks and spots do not show. Obviously also the coloring matter should have no effect on the silver salts, nor be itself affected by the photographic solutions.

The following is taken as a typical mixture and method of mixing:

Medium gelatine	550 g
Distilled water	6500 ccm

Soak the gelatine overnight in the water. If any color is to be added, which is usually done in the third coating only, 1000 ccm of the water should be set on one side for its solution or admixture. Melt the gelatine in a water bath at 45° to 50° C. (113° to 122° F.) and filter through a filter cloth. Add to:

Glossy baryta paste, 56%	12000 g

As already pointed out, the usual water content of the paste must be determined and for use mixed with enough more water to give a paste containing 56 per cent of dry barium sulphate and 44 per cent of water. It is important to add the gelatine solution to the baryta and not the reverse. Care must be taken to intimately mix the two. The old method and one that is still considered by some workers as the only correct way, is to mix with the hands; but special mixing machines are preferable.

To the thoroughly mixed baryta and gelatine should be added:

Chrome alum, 10% solution	350 ccm
Glycerin, sp. gr. 1.20	50 ccm

After this has been thoroughly worked in, add:

Alcohol, 95%	500 ccm

Alcohol denatured with phenol may be used. Then there should be worked in:

Fresh milk	100 ccm

This addition is used to prevent too much frothing. It must be quite fresh and should be heated three times to boiling, taking care not to burn it.

For printing-out papers, it is very usual to add to the above, immediately after mixing the baryta and gelatine:

Citric acid, 10% solution .... 100 ccm

The total weight of the above should be about 20 kilos.

In coating, 1000 g of the baryta mixture, as above, is required for every 10 square meters of paper surface for the three coats. But as it is necessary to allow for some waste in filtering and coating and it is impossible to use the last drop in the coating trough, roughly one-fifth more than the above quantity should be allowed.

The mixture should be filtered again and heated to 45° to 50° C. (113° to 122° F.) to give the correct coating temperature of about 41° C. (105° F.). The coating speed should be 28 meters per minute.

When the paper has received its three or more coatings and has been calendered, it should be allowed to stand at least eight days, and if possible six weeks, before use, so as to allow thorough hardening of the gelatine. It is important also that the rolls should not rest on anything, otherwise the paper will be deformed by its own weight. The rolls should be suspended by the ends of the mandrel passing through the center core.

As a test for the suitability of the baryta coating, the following may be used: a strip of paper, about 30 cm long and 2½ to 3 cm wide should be fastened to a glass rod and suspended for five minutes in a 500 or 1000 ccm glass cylinder, filled with distilled water at 40° C. (104° F.), then slowly withdrawn, taking care not to let it touch the sides of the cylinder. By allowing the cylinder to stand for an hour, one can estimate by the quantity of baryta precipitated how it will stand the warm emulsion, etc.

For P. O. P. or gelatine-chloride printing-out paper, the following specific formula is recommended:

Glossy baryta paste, 56%	12000 g
Hard gelatine	500 g
Water	5000 ccm
Denatured alcohol	500 ccm

This should be prepared as described above and hardened with:

Chrome alum, 10% solution	300 ccm
Glycerine	15 ccm

For the cheaper classes of papers, two coatings of the above mixture are sufficient, and four coatings for the better class.

For collodio-chloride emulsions the following coatings are given in tabular form:

	I	II	III	IV	V
Glossy baryta paste, 56%	12375 g	12375 g	12375 g	——	3275 g
Matt baryta paste, 66.6%	——	——	——	2700 g	3275 g
Barytes (1)	——	——	——	2700 g	——
Gelatine	300 g	600 g	300 g	600 g	550 g
Pale glue (2)	400 g	——	400 g	——	——
Water	6625 ccm	6125 ccm	6125 ccm	9000 g	6480 ccm
Citric acid, 10% solution	——	——	——	100 ccm	100 ccm
Alcohol, 95%	——	——	——	1600 ccm	1600 ccm
Hardener (3)	480 ccm	480 ccm	480 ccm	580 ccm	580 ccm
Milk	300 ccm	300 ccm	300 ccm	75 ccm	75 ccm
No. of coatings	4	4	4	3	3
Total weight required to coat 1000 m paper 66 cm wide	68 kilos	68 kilos	68 kilos	56 kilos	59 kilos

I. This is for glossy cards for combined toning and fixing baths. II. For glossy paper for separate baths. III. For glossy paper for combined baths. IV. For matt paper. V. For half-matt paper. (1) This is dry barium sulphate, made into 66.6% paste with water. (2) The glue facilitates toning in combined baths, but easily causes red spots in separate baths. (3) This is 10% solution of chrome alum, containing 1.8% of glycerine.

TABLES. — The following tables will be found useful in emulsion calculations. The first enables the operator to calculate the weight of alkaline halide necessary to convert any given quantity of silver nitrate or vice versa; also the quantity of silver halide produced from every part of the alkaline halide or silver nitrate. Also the excess of alkaline halide. For instance, suppose we have a formula as follows:

Ammonium bromide	475
Potassium iodide	10

The quantity of silver nitrate required to saturate these will be

Ammonium bromide	475 × 1.734 =	823.650
Potassium iodide	10 × 1.023 =	10.23
		833.880

The quantity of silver bromide produced will be

475 × 1.918 = 911.051

and the quantity of silver iodide

10 × 1.415 = 14.15

The second table enables one to replace one halide by another. For instance, taking the same weight of ammonium bromide as above and assuming that we want to use the corresponding potassium salt, we find by referring to the first figure column that we must use

10 × 1.415 = 14.15

In the same way, if ammonium iodide is to replace the potassium salt, on referring to the column headed "potassium iodide," we find that we must use

$$10 \times .873 = 8.73$$

of the ammonium iodide.

RATIOS OF HALIDES AND NITRATE

	Molecular Weights	Weight of $AgNO_3$ required to convert one part of alkaline halide	Weight of soluble halide required to convert one part of $AgNO_3$	Weight of silver halide produced by one part of soluble halide	Weight of soluble halide required to produce one part of silver halide	Weight of silver halide produced from one part of $AgNO_3$
Ammonium bromide.	98	1.734	.576	1.918	.521	1.106
Potassium bromide..	119	1.427	.700	1.578	.633	
Sodium bromide.....	103	1.620	.606	1.825	.548	
Ammonium chloride.	53.5	3.177	.315	2.682	.373	.844
Sodium chloride	58.5	2.906	.344	2.453	.408	
Ammonium iodide ..	143	1.172	.853	1.620	.617	1.382
Potassium iodide....	166	1.023	.977	1.415	.707	
Sodium iodide.......	150	1.133	.882	1.566	.638	

EQUIVALENCE OF OLKALINE HALIDES

	Ammonium bromide	Potassium bromide	Sodium bromide	Ammonium chloride	Sodium chloride	Ammonium iodide	Potassium iodide	Sodium iodide
Ammonium bromide....	1	.823	.951	1.832	1.675	.676	.590	.653
Potassium bromide.....	1.215	1	1.156	2.226	2.036	.821	.717	.794
Sodium bromide.......	1.051	.865	1	1.925	1.761	.710	.620	.684
Ammonium chloride....	.546	.449	.519	1	.914	.369	.322	.356
Sodium chloride.......	.597	.491	.568	1.093	1	.403	.352	.390
Ammonium iodide.....	1.479	1.217	1.408	2.712	2.478	1	.873	.966
Potassium iodide.......	1.695	1.394	1.612	3.104	2.839	1.145	1	1.107
Sodium iodide.........	1.530	1.259	1.456	2.803	2.564	1.034	.903	1

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[1] *Brit. J. Phot.*, 1913, **60**, 734.

[2] *Phot. News*, 1881, **25**, 356.

[3] *Ibid.*, 1882, **26**, 310.

[4] *Brit. J. Phot.*, 1882, **29**, 474.

[5] *Ibid.*, 1884, **31**, 685.

[6] *Photography with Emulsions*, 1882, 170.

The History of Three-Color Photography

By

E. J. WALL, F.C.S., F.R.P.S.

Author of "Practical Color Photography," "Photographic Facts and Formulas," "Carbon Printing," "Dictionary of Photography," etc.

FOR over thirty years Professor Wall has been searching out the original literature of color photography and allied subjects in technical books and magazines, and making detailed notes for use in his own research and consulting work. With the lapse of years the bulk of the material became so great that he decided to put it in orderly form, and so rewrote his notes into a manuscript covering every phase of color work, and extending to several hundred thousand words. Practical considerations have forced the omission of some parts of the original manuscript from the present volume, which does not deal with the Lippmann, Seebeck or Bleach-out processes or with photomechanical reproduction. With these exceptions, the work attempts to record every step in the progress of color photography of both still and moving subjects to the most minute detail. Subject by subject, the whole field is reviewed from the most remote period to the early part of 1925, with detailed references to the original article or patent specification in every case. Not only are articles and patents, which by their titles appear to refer to the subject, abstracted, but a great number of indispensable references to material, published under headings apparently far removed from color photography, are included. The patents of all the leading countries have been thoroughly searched, and in color cinematography, where there is practically no literature, the results are of the highest importance. In all some 9,000 original articles and 3,400 patents are referred to, and the result of this enormous labor is a volume which exhausts its subject as no book on photography has yet done. Every serious experimenter will find that it opens to him all that has ever been done on the subject. He will not only find here the road to success in studying the now-used methods and processes, but he will discover multitudes of

The History of Three-Color Photography
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