MAKING PHOTOGRAPHIC EMULSIONS

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So far as the writer is aware there have been two books in the English language on photographic emulsions: Abney's "Photography With Emulsions" (1885) and E. J. Wall's "Photographic Emulsions" (1929). There was also Wall's translation of Eder's volume on "Photographie mit Bromsilber-Gelatin und Chlorsilber-Gelatin," which appeared in a journal as far back as 1892.

There is, however, a very large literature on various phases and problems of emulsion making, but it is hidden away in scientific and technical publications, and only with difficulty is it available to the average student. Moreover, a large proportion of it is in French, German, or some other foreign language. It is, perhaps, a result of this state of affairs that a legend appears to have grown up, by which the making of photographic emulsions is conceived as a very difficult and mysterious operation hedged round by all sorts of taboos, and involving the use of secret formulæ and processes, details of which have never seen the light of day.

This is all wrong; photographic emulsions are quite easy to make. Anyone who can purchase the raw materials and has access to a few simple pieces of apparatus can produce photographic emulsions. What they cannot produce are consistent results, high quality and high sensitivity. Hence they cannot and never will be able to compete with the highly trained and organised and scientifically controlled manufacturer's staff who are compelled to turn out emulsions of the highest quality and sensitivity with absolute consistency all the year round, and who must be able to so control their product that they can produce to an exact as well as to an exacting specification.

So it happens that except for the books mentioned above, all other works which refer to emulsion making content themselves with a bare outline of the process without any details, a procedure which is somewhat aggravating to the would-be experimenter who has no intention of emulating the manufacturer, but who would like to prepare a comparatively simple emulsion if only reasonably detailed instructions were available to allow of his doing so.

In the present article such information will be provided, but it will be preceded by a sketch of the emulsion making process as generally practised on a manufacturing scale, with some discussion of the factors which influence the properties of an emulsion and which exert their influence, whether the emulsion is being made by the few ounces or the hundred gallons.

Later, recipes will be given for the making of several types of emulsion for both negative and positive processes. These should provide a starting point for any experimenter who desires to try his hand in this direction. If any success is to be attained rigorous control and accurate testing are essential and the extent to which these are attained will determine the measure of that success.

Manufacturing Emulsions.

In this section we shall confine ourselves to gelatine emulsions, and take for granted that the reader knows that the so-called photographic emulsion is in reality a suspension of grains of a silver salt, usually called a silver halide, that is a halogen salt of silver, i.e., a bromide, chloride or iodide, in gelatine.

A word or two about the vessels used by the manufacturer; glass and stoneware are used as receptacles, but metals are being more widely used now that certain stainless steels and metals such as " Inconel " have been found innocuous. Years ago if metals were used they were very heavily silver plated or were of silver itself. All jars or similar receptacles have light tight lids and extra precautions are taken if these receptacles have to be brought out into white light.

The actual process of emulsification generally consists in the addition of a solution of silver nitrate to a solution of gelatine containing the bromide, chloride or iodide, or the mixture of salts required. As is well known, the presence of the gelatine prevents the formation of a precipitate or its falling to the bottom of the vessel. What is formed is a thick creamy suspension which we call the emulsion. In the case of emulsions intended for plates or films, bromide predominates, but iodide is usually present in proportions varying from a ratio of 1 : 15 to 1 : 25 to the bromide. The function of the gelatine at this stage of the process is to ensure a fine suspension and as a rule the amount is about one-fourth of what will actually be present in the emulsion when finished. Gelatine can and does act to some extent as a sensitizer, but its action in this direction is much less than that of other substances added at the next stage in the process. The emulsifying gelatine, as it is called, may amount to anything between 2 per cent. and 5 per cent. of the whole ; generally the amount is dependent upon the character of the emulsion and the method of emulsification used. In commercial practice there are very few exceptions to the rule that the ratio of silver salt to bromide or other halide shall be such that an excess of halide is present at the close of the emulsification process. This is ensured by making use of the equivalents of silver nitrate and the halide salts, and as such tables are not always easily available to the photographer we note here that 1,000 parts of silver nitrate are the equivalent of 701 parts of potassium bromide, 576 parts ammonium bromide, 344 parts of sodium chloride or 315 parts of ammonium chloride and 971 parts of potassium iodide. By ensuring that the proportion of halide salt is always in excess of these equivalents for every 1,000 parts of silver nitrate used an excess of halide over silver salt is obtained. The way in which the silver is added to the bromized or halogenized gelatine is important. It may be poured *en masse*, or as it is usually called " dumped," or it may be run in slowly through a tube with a small orifice. In either case the emulsion is kept stirred throughout the whole operation of emulsification. It is now ready for the process of ripening upon which will depend in no small degree its final sensitivity. In the olden days there were two general methods of preparing emulsions which were known as the acid or boiling process and the alkaline or ammonia process. To-day the latter has almost entirely superseded the boiling method. Ripening, as it is called, depends upon the emulsion being kept at a particular temperature for a specified time during which the ripening agent can act. This agent in the case of boiled emulsions was usually ammonia, with sometimes thiocyanates as well. In the ammonia emulsion the name indicates that ammonia was the ripener.

Ripening completed, the first stage of the emulsion making process concludes with the setting off of the emulsion either in a cold water tank, or one in which melting ice keeps the temperature to just about freezing point. The setting off is a preliminary to the washing of the emulsion to remove the soluble and unwanted salts produced by the action of the silver nitrate on the halide. The first step toward washing is the shredding of the set emulsion. In the works this is usually done in a hydraulic press which forces the emulsion through a press plate. The whole process has affinities on a large scale with the household mincing machine, the emulsion being forced through the holes of the press plate and so converted into shreds or "worms" which offer a large surface to the water and so are more easily washed. The time of washing is important, as also the temperature and the alkalinity or otherwise of the wash water. If washing is too prolonged the gelatine suffers; equally if the water is much on the alkaline side then prolonged washing will mean fog. Acid wash waters mean loss of sensitivity, so it will be realised that the process of washing is one into which careful control enters. A number of the early gaslight emulsions were not washed at all, but to-day it is the rule to wash all gelatine emulsions. Various methods are used to bring about intimate contact between the shreds and the wash water. Revolving receptacles with canvas or other mesh openings have been used. Silvered wire baskets immersed in vessels through which water flows and even canvas bags in which the shreds are placed have all played a part. The washed shreds are allowed to drain and are then re-melted in preparation for the next stage, which generally involves the adding of more gelatine and a process which is known as digestion. The amount of gelatine added at this stage is usually about double the quantity used for emulsification. Sometimes it is added as sheets or powder to the melted emulsion and stirred until dissolved, at other times it is swelled with water first and then added. In the case of some paper emulsions the melting and addition of gelatine represent the last operations of making, and the emulsions can be taken to the coating room, and after the addition of what are called the coating doctors, they are coated. A word about these "doctors." They comprise spirit, usually ethyl alcohol, preservatives such as phenol, thymol or the like, and solutions such as soap-bark or quillaia which increase the wetting power of the emulsion and so help even coating. In the case of emulsions used for plates or films the procedure is usually very different, for the emulsion is usually digested with a further quantity of gelatine for a period which has been shown to confer the sensitivity and possibly also the gradation required. At the close of the digestion period a further quantity of gelatine is often added. This is known as the bulk or finishing gelatine. With the exception of the coating doctors the emulsion now only requires preservatives adding, and can be either sent to store or coated. Even with so bare an outline as this it will be obvious that every stage of the process involves the most careful and accurate control, because every stage has its specific purpose and end. So far nothing has been said about colour sensitizing or otherwise varying the properties of emulsions by additions other than preservatives.

The reason is that such additions are almost invariably added just before coating, and so are not really a part of the emulsion making process. In the case of plate and film emulsions sensitizing dyes to produce orthochromatic or panchromatic results are now available to anyone, and in very different quality to what was once the case. The study of sensitizing dyes has now provided the manufacturer with a range that permits of sensitizing to practically any part of the spectrum from the near ultra-violet to the comparatively far infra-red ; nor is this all, for to-day we have a number of chemicals available, known as improvers, which can notably affect the keeping properties, tendency to fogging and other properties of emulsion in a very remarkable manner. Many of these are specially applicable to paper emulsions and are designed to produce desired or desirable image colours, confer a particular gradation or increase the normal latitude of the paper to development.

Making Experimental Emulsions.

In this section we shall consider the making of several emulsions such as are actually used in the photographic industry. They will represent types such as a film negative emulsion, a bromide paper and a gaslight paper. It will not be expected that the details will be exactly those used by any particular manufacturer. It is not possible to translate bulk methods into very small units, but the recipes given will provide working emulsions if properly carried out and will serve as examples of how the types differ and give a general idea of the procedure adopted in making emulsions.

One or two points must be noted first. A good dark room is essential. No one should attempt to prepare emulsion unless they have a good dark room permanently at their disposal. As to apparatus, this is simple enough. Porcelain beakers or stoneware jars of a pint or quart capacity, fitted with well-fitting light tight lids, can be used for emulsifying, etc. The beakers are best for melting, digesting, and the like, because of their thinner walls. All this work has to be done in a water-bath, and a reasonably capacious water-bath, preferably with some sort of thermostatic control, is also an essential. A refrigerator is a luxury, but a good sized tank with running water which can be used for cooling and setting off is a necessity. Washing of emulsions calls for a shredding machine, and for this a well enamelled household mincing machine will suffice. If the perforated plate is not also enamelled it must be of stainless steel. It should produce shreds about $\frac{1}{8}$ of an inch diameter.

Washing may be done in a linen bag or in a small hair sieve, which can be held under the surface of the water. Running water is not essential. Eight or ten changes of water at intervals of about five minutes with a couple of minutes drain between each should be sufficient for most experimental emulsions. Other details of manipulation will be dealt with as they arise. Quantities will be in grams and cubic centimetres. Note that if avoirdupois quantities are required make use of the convention 1 gram = 20 grains and 1 ounce = 25 grams or, if fluid, c.c.s. While not exact it is quite near enough for the work in hand and saves troublesome calculations.

As to gelatine, a good photographic quality is essential, and the one usually available is Nelson's leaf. Whereas various gelatines are used by the manufacturer the experimental emulsion maker will probably have to be satisfied with one. It must not be expected that a speed number can be given for these experimental emulsions. Their speeds will have to be determined by the maker when they are finished, and it is more than likely that the speeds will vary greatly with each lot made.

NEGATIVE EMULSION FOR PLATE OR FILM.

This is a normal ammonia emulsion of fair speed and good gradation.

Solution A.	Gelatine	15 gms.
	Water	200 c.c.s.
	Ammonium bromide... ...	25 gms.
	Potassium iodide	1 gm.

First swell the gelatine in the water, then raise temperature to 125° F, stir in the two salts and dissolve, keeping temperature at 125° F.

Solution B.	Silver nitrate	30 gms.
	Water (distilled)	100 c.c.s.

Raise water to 100° F, then add nitrate and stir until dissolved. Then bring temperature to 105° F and pour the whole of solution B (silver) into solution A (bromide gelatine) quickly. Stir well for about *two* minutes and then add 4 c.c.s. of ·880° ammonia diluted with 10 c.c.s. of water. See that temperature is now maintained at 125° F for 40 minutes, then set off on ice or in running water in thin walled vessel to cool quickly. When fully set, shred and wash for one hour or in 8-10 changes of water, and add when dissolved :—

Gelatine	20 gms.
Water...	100 gms.
Spirit (alcohol)	10 c.c.s.

Swell the gelatine in the water, raise to 120° F, add spirit, then stir into emulsion when fully melted. Now digest for one hour at 125° F and then add the following.

Gelatine 25 grams dissolved in 100 c.c.s. water to which 10 c.c.s. of spirit and 25 c.c.s. of a 2½ per cent. solution of carbolic acid in spirit has been added. The emulsion can now be coated or stored as desired.

It is probable that the emulsion will be coated on glass plates, if so care must be taken to ensure that the plates are scrupulously clean. As an extra precaution it is always worth while to clean the glass with the bichromate-sulphuric acid mixture, using the precautions which this violently corrosive mixture requires. For the actual coating a small teapot, or invalid feeding cup with a thin spout, is the best utensil for pouring. Temperature must be sufficient to ensure perfect fluidity and should be about 100° F.

When melted for coating the hardener can be added. This is usually chrome alum, and the proportion can be taken as 1 gram for every 1,000 grams of finished emulsion. Hence, if you have 1,000 grams of emulsion add 10 c.c.s. of a 10 per cent. solution of chrome alum in water, adding it very slowly and stirring it all the time.

If sensitizers are to be added they come in at this stage. The best orthochromatic sensitizer for the experimenter to use is erythrosin (tetra-iodo-eosin), in the proportion of one-tenth of a gram per 1,000 grams of emulsion. The erythrosin is best added as an alcoholic solution of 1 per cent. Hence for 1,000 grams of emulsion 10 c.c.s. of the dye solution should be stirred in carefully about 15 minutes before coating.

The plates are coated one by one by pouring sufficient emulsion in a pool in the centre of the plate to cover the whole plate when carefully tilted so as to obtain an even flow over the whole plate. Any excess is poured off into a waste receptacle, not back into the coating vessel. As soon as coated the plate should be laid on a plate glass or slate slab to set, and then dried in a current of preferably filtered air. All these operations are naturally carried out in a safe light or in darkness.

Bromide Paper Emulsion. Slow Normal Type.

Solution A.	Gelatine	15 gms.
	Potassium bromide	40 gms.
	Potassium iodide	1 gm.
	Citric acid	40 gms.
	Water	200 c.c.s.

Soak the gelatine in the water until swelled, then raise the temperature to 120° F, and dissolve the bromide and other salts in the order given. Cool to 90° F and pour solution B into solution A.

Solution B.	Silver nitrate	50 gms.
	Water	350 c.c.s.
	Ammonia ·880°	Sufficient

The silver is dissolved in the water; if warmed the solution is now cooled and sufficient ammonia added, drop by drop, to just redissolve the precipitate at first formed. Now warm to 90° F and dump into solution A, stirring well the whole time. Now heat the emulsion slowly until it attains 120° F, which should be in about 20 minutes. Now add 15 grams gelatine, dissolved in 60 c.c.s. water, and also at 120° F and set off. Wash when ready, drain well, melt at 100° F, add a further 40 grams of gelatine dissolved in 160 c.c.s. water already at 120° F., then add 50 c.c.s. spirit and 5 c.c.s. 10 per cent. chrome alum solution and coat. Coating is carried out by dipping the paper on to the surface of the melted emulsion in a deep dish. A little practice soon enables coating to be made at about the right thickness. Temperature and speed at which the paper passes over the emulsion are the important factors. Coating temperature not less than 100° F.

Gaslight Paper Emulsion. Slow Vigorous Type.

This is a somewhat old-fashioned type of gaslight emulsion, giving clean, vigorous quality and average to slow speed. Three solutions are first prepared separately as follows :—

Solution A.	Gelatine	16 gms.
	Water	150 c.c.s.
Solution B.	Silver nitrate	15 gms.
	Water	80 c.c.s.
Solution C.	Ammonium chloride ...	7 gms.
	Copper chloride	½ gm.
	Hydrochloric acid conc. ...	2 c.c.s.
	Water	25 c.c.s.

Make up all three solutions and bring them to 95° F. Then pour B into A and stir well, then at once dump C into the well-stirred mixture of A and B. Set off to cool slowly. Next day shred, wash and drain. Then melt at 90° F, bring up to 110° F, and add :—

Gelatine	30 gms.

stirring quietly until gelatine is wholly dissolved. Then add 20 c.c.s. spirit, 5 c.c.s. 10 per cent. chrome alum. Stir well. Bring temperature down to 95° F and coat.

Note that neither in the case of the bromide nor of the gaslight emulsions have normal coating doctors been mentioned. The reason is that for small experimental quantities such as are indicated they should not be necessary.

The three examples that have been given illustrate three quite different types of emulsion, and also three different methods of making. The negative emulsion might almost be called the orthodox negative emulsion type. The bromide emulsion really belongs to the acid or boiled emulsion type, and is sometimes spoken of as the converted silver class of emulsion, meaning that the silver nitrate has been treated with ammonia before emulsification has taken place. Needless to say endless variations can be made on these three themes. Just how such variations can affect the final result must be left for the experimenter to discover. If he does desire to make variations then he should remember that only one factor must be varied at a time, otherwise the result will not be variations, but chaos. It may not be amiss to quote a paragraph from the preface to E. J. Wall's book on emulsions. "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." Of this, the present writer has to say that E. J. Wall was a gifted experimenter and that he is in the fullest agreement with the remarks contained in the above quotation.

Finally, it may be noted that there are occasions, particularly in scientific and technical work, where a non-sensitized emulsion is required for experimental work, it may be to test the sensitizing or perhaps even the desensitizing properties of substances, or it may be to determine the stabilizing qualities of some particular chemical. In such cases the negative emulsion given here may be useful because it is very simple to make and with reasonable care can be duplicated time after time, a matter of great importance when experiments extend over a long period as they well may do.

For experiments on gradation and gradation control either the bromide or the gaslight emulsion can be used, and as both are typical of their group results obtained on them will apply generally to similar emulsions.

Note that if a slow emulsion of positive type is wanted for lantern slides then the gaslight formula is suitable ; it provides an exceedingly fine grain emulsion. In such a case the washed shreds should be melted at 90° F. and the extra gelatine added at that temperature and stirred until dissolved. This in place of raising the whole to 110° F. as given above.