

PHOTOGRAPHIC EMULSION TECHNIQUE

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PHOTOGRAPHIC EMULSION TECHNIQUE

BAKER

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TABLE OF CONTENTS

INTRODUCTION	ix
I. NATURE OF PHOTOGRAPHIC EMULSIONS	i
Introductory — Light-sensitive Silver Compounds — The Nature of an Emulsion — The Function of Ammonia — Sensitizing Properties of Gelatin — Ostwald Ripening — The Crystal Structure of Silver Bromide — Iodide in Emulsions — Grain Size and Emulsion Characteristics — The Effect of Light on Silver Bromide	
II. MATERIALS FOR EMULSION MAKING	21
Gelatin — Chemicals and Their Choice — Analyses and Tests — Storage — Methods of Handling Bulk Materials	
III. LABORATORY EQUIPMENT	37
Layout for Experimental Work — Commercial Production and Its Requirements — Ventilation — Safelights — Digesting Apparatus — Thermostatic Control — Washing and Filtering of Emulsions — Making up — Cold Storage	
IV. NEGATIVE EMULSIONS	63
Their Structure and Composition — Types of Formula — Preparation of the Reacting Solutions — Emulsification — Ripening — Setting — Washing — Final Digestion or Finishing — Making up — Anti-halation Methods — Reversal Emulsions	
V. SLOW EMULSIONS	86
Sensitive Material for Copying, Commercial Work and Transparencies — Methods of Producing High Resolution and Fine Grain —	

	Chloro-bromide Emulsions — Chloride Emulsions — Mixed-jet Emulsification — Development of Warm Tones	
VI.	COLOR-SENSITIVE EMULSIONS	103
	Action of Color-sensitizers — Orthochromatic and Panchromatic Plates and Films — Self-filtering Emulsions — Hyper-sensitizers — Bipacks and Tripacks — Three-layer Color Films — Dye-couplers and Color Formers	
VII.	X-RAY AND ULTRAVIOLET	128
	X-ray Emulsions — Intensifying Screens — Lippmann Emulsions — Ultraviolet Plates	
VIII.	COATING EMULSIONS ON GLASS	138
	Preparation and Cleaning of the Glass — Substratums — Drying Cupboards and Drying Problems — Coating Heads — Ventilation and Heating	
IX.	BROMIDE AND CHLORIDE PAPERS	155
	Nature of the Raw Paper — Paper Tests — Baryta Coating — Emulsion Formulas — Laboratory Methods of Coating and Drying — Commercial Coating Machines — Drying Tunnels — Non-stress Coating — Drying, Reeling and Packing — Variable Contrast Papers	
X.	FILMS, NEGATIVE AND POSITIVE	175
	Types of Base — Substratums — Substratuming Machines — Negative Film Emulsions — Positive Film Emulsions — Experimental Film Coatings on Roll and Cut Film — Film Coating Plant — the Drying Tunnel — Air-conditioning — Films for Imbibition Emulsions — Static — Commercial Defects — Packing	
XI.	PRINTING-OUT EMULSIONS	192
	Salted Paper — Sensitizing Silk — Printing-out	

TABLE OF CONTENTS

vii

Emulsions — Gelatino-chloride Papers — Collo-
dio-chloride Papers — Self-toning Papers — Sil-
ver Phosphate Papers

XII. TESTING EMULSIONED PRODUCTS	202
Testing Equipment — Estimation of Speed and Quality — Interpretation of the Characteristic Curve — Measurement of Color-sensitivity — Photometers and Density Meters — Keeping Tests	
XIII. VARIOUS METALLIC PROCESSES	236
Carbon and Carbro Tissue — Gum-bichromate — Iron Printing Processes — Ferroprussiate — Cyanotype — Kallitype — Platinotype and Pal- ladiotype — Diazotype Papers — Bleach-out Color Processes	
XIV. EXTREME-SPEED EMULSIONS	253
Super- and Hyper-sensitizers — Sulphur Com- pounds in Gelatin — Anti-fogging Agents — Speed Characteristics	
INDEX	259

INTRODUCTION

THE pioneer days of photography were noteworthy for the fact that the sensitive material which recorded the camera image was in a state of continual evolution. The dramatic change from collodion to gelatin emulsions due to Dr. Maddox in 1871, introduced a new era in the art of photography because of the mysterious increase in speed which the use of gelatin brought about. Although so many years elapsed before the nature of the gelatin sensitization was discovered, empirical work with gelatin emulsions brought about a constantly increasing sensitiveness to light, which culminated in the early part of this century in a speed of about 400 H and D, or its equivalent of 10 Weston. Twenty years later the speed of photographic plates jumped up to half as much again, and after another twenty years modern color-sensitive emulsions with their super-sensitizers made another remarkable jump to something between five and ten times the old figure.

In the meantime, the application of photography to technical, industrial and scientific problems has expanded on a truly amazing scale which needs no emphasis here. Physical chemists, physicists and mathematicians have been attracted by the fascinating nature of the phenomena associated with sensitive emulsions into a new field, with which this book attempts in some part to deal.

During an experience of more than thirty-five years in the emulsion-making field, the author has been approached on numerous occasions with requests for sources of information on photographic emulsions. In many branches of experimental work and scientific research, it is felt that it would be of un-

doubted benefit and convenience if serviceable emulsions could be made on a laboratory scale, and suitably coated. As time proceeds, many newcomers enter the field of commercial production of one kind or another, and in the following pages the problems of the investigator and the manufacturer are fully discussed. The investigator is obliged to buy in the open market the available material which happens to possess characteristics nearest to his requirements. The factory laboratory, on the other hand, makes a considered choice of materials and checks up on that choice with manufacturing scale tests. Apart from actual manufacture, the making of emulsions provides a scope for experiment pregnant with possibilities. Some knowledge of emulsion chemistry is of the greatest value in the general study of photographic processes.

In the pioneer days, photographers had to make their own emulsions, and it was by the combined efforts of a small coterie of experimenters at the end of last century that the modern "dry plate" came into being. Some of these men were pure amateurs, others were practical chemists and men of scientific training. Out of this little band of experimenters came the founders of most of the original commercial emulsion-coating factories. The inevitable then happened. The businesses came into competition with one another, and further advances gradually became guarded as trade secrets. There came a spectacular lull in the hitherto prolific literature, and the textbooks of Dr. J. M. Eder and Sir William (then Captain) W. de Wivesleigh Abney were the chief fodder on which the would-be experimenter had to feed.

The interest in emulsion chemistry was renewed in 1920 and onwards. The classic work of The Svedberg and other distinguished physicists introduced new methods of attack on the morphology of the silver halide grain. A little later, at a Paris Meeting of the International Congress of Photography, Dr. S. E.

Sheppard announced his discovery of the effect of the presence in gelatin of allyl isothiocyanate — the secret of speed had been revealed. But the millennium had not arrived, for speed could not be increased *ad libitum* by just increasing the proportion of sensitizer used in the preparation of the emulsion.

The sensitiveness to light of the emulsion depends to quite an important extent on the particular gelatin used, and its inherent "impurities." But it is also dependent on the method of precipitation of the silver halides, on the method and degree of ripening, and on the digestion which the emulsion receives after the by-products and excess solvents of silver bromide have been removed by *washing*. Modern technique, however, makes it possible to control within fairly definite limits the character of an emulsion, so that by predetermined conditions the manufacturer can produce a plate or film having a long scale of gradation for the pictorial photographer, a process film suitable for line work, an emulsion specially responsive to X-rays, a soft-working bromide paper for enlargements, or a contrasty chloride paper for the photo-finisher. Add to this the power which Vogel's discovery of color-sensitizing gave to the industry, and we find a further field for experiment of vast potentialities, which has helped of course in large measure to provide the various solutions to the problem of natural-color photography, and to improve the graphic arts.

While the amateur emulsion-maker cannot compete with the manufacturer of sensitive materials, the latter cannot be expected to interrupt works routine by supplying small coatings of experimental emulsions made to some specification outside his own range of products. This book is thus intended not only to be a guide to practical emulsion making, but as a textbook for technical students, industrial chemists and photographers generally, who are anxious for their own reasons to prepare emulsions of various types and speed. With careful work, ex-

cellent results of repeatable quality can be made on a small laboratory scale, and the apparatus involved need be neither elaborate nor costly.

The great majority of formulas given in the following pages have been quoted from published communications, but it has been the special aim of the author to set out the fundamental lines upon which such formulas are based, so that the emulsion-maker can construct his own for any desired purpose. New needs for special characteristics crop up with great frequency, and there is definite scope for the manufacturer of sensitized products who is able and willing to meet these new demands, which may not necessarily run into immense production figures.

The manufacturer is helped today very largely by modern air-conditioning equipment, improved means for temperature control, excellent emulsion-making plant and coating machinery, and above all by the splendid researches in emulsion chemistry which have been carried out in recent years. With the further help of modern sensitometric work, special packing materials, checking by trained technicians, and above all the ever-growing intelligence of the photographer himself, the sensitive materials industry has reached a high state of efficiency, and its products have assumed the character of precision instruments.

Grateful acknowledgments are given to the Research Laboratories of Eastman Kodak Company, and Kodak, Ltd., for photographs kindly supplied; also to Messrs. T. H. Dixon and Co., Ltd., and Messrs. W. Watson and Sons, Ltd., for illustrations of plant and apparatus; to Burt H. Carroll and Donald Hubbard, whose research papers have been frequently quoted; and to Mr. Charles A. Silver for his assistance with the proofreading.

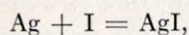
CHAPTER I

NATURE OF PHOTOGRAPHIC EMULSIONS

Introductory — Light-sensitive Silver Compounds — The Nature of an Emulsion — The Function of Ammonia — Sensitizing Properties of Gelatin — Ostwald Ripening — The Crystal Structure of Silver Bromide — Iodide in Emulsions — Grain Size and Emulsion Characteristics — The Effect of Light on Silver Bromide

THE image formed by the lens of a camera is recorded on a light-responsive surface which in present-day photography takes the form of sensitive silver salts in a film of gelatin. No visible action takes place in this film during a normal exposure. But it is capable of providing ultimately a visible and permanent image, obtained in practice by developing the invisible or *latent* image formed by the action of the light-rays in exposure. Daguerre showed that by exposing in the camera a plate made of polished silver treated with iodine vapor, an invisible latent image was formed which could be rendered visible by development with mercury vapor. The mercury deposits itself on the parts of the surface exposed to light, but does not adhere to the unexposed parts. The first reference to photographic sensitometry was probably made by Arago in his statement that "to the portions which represent the halftones the mercury affixes itself in greater or less quantity proportional to the action of the light upon these parts."

The thin film of silver iodide formed by the action of iodine vapor on silver, according to the equation



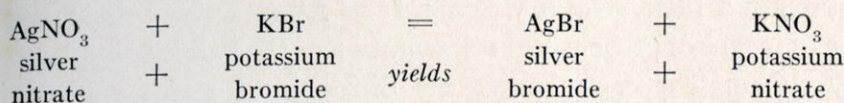
was in no sense an *emulsion*, but merely a stain similar to the discoloration of a brightly polished silver article exposed to the sulphurous atmosphere of a city. The approach was nev-

ertheless being made towards the emulsion, but it was years later when Niépce de St. Victor coated glass plates with a mixture of albumen and starch in which were suspended the sensitive salts. Three years later came the wet-collodion process. In this, a solution of guncotton dissolved in ether and alcohol and containing soluble bromide and iodide was poured over a glass plate and sensitized by flowing a solution of silver nitrate over the set, but still damp, collodion film. The plate was exposed immediately in the camera, so that the soluble excess salts should not crystallize out.

In an effort to cut out the sensitizing process (still largely used today), the first actual emulsion was produced. This was a suspension of silver bromide or iodide in collodion, made by Bolton and Sayce. Then came the use of gelatin by Dr. Maddox, and today we find that the great bulk of sensitive photographic materials consist of gelatin "emulsions," or suspensions of silver salts in a solution of the protective colloid *gelatin*, applied to glass, celluloid or cellulose acetate film, paper, and more recently to thin aluminium alloy sheets.

It will thus be gathered that a modern photographic emulsion consists of a suspension of silver halides in gelatin, which is applied to a suitable support. It should be noted that emulsions have been made by Staud and Connelly by dispersing the silver halide in a mixture of gelatin and a water-soluble cellulose ester such as cellulose acetate or lactate,¹ while Sheppard and Houck have used the potassium salt of cellulose acetate diphthalate.² Agar-agar has been employed with little success. In spite of wide research, no compound or substance has yet been discovered which is anything like as sensitive to light as bromide of silver, yet extreme sensitiveness can be obtained only when it is subjected to the influence of gelatin, and if chemical fog is to be avoided on development, a small proportion of the iodide of silver must accompany the bromide.

The salts are formed by double decomposition, as for example:



While from the chemical equivalents it would seem that 170 parts by weight of silver nitrate would react with 119 parts of potassium bromide, it is necessary in practice to have present an excess of soluble bromide, for reasons which will be discussed later. If an excess of silver *nitrate* were present, then the emulsion would print out on sufficient exposure to daylight, giving a visible image of metallic silver; for this purpose, however, the chloride of silver in combination with an organic silver salt is commonly used. Silver chloride without excess of silver nitrate gives, on the other hand, a comparatively insensitive emulsion of the type used in making chloride or "gaslight" papers and slow transparency plates, which yield on alkaline development black and white images having great contrast and brilliance.

Thus the three halides, silver bromide, chloride, and iodide, suspended in gelatin or other suitable colloid medium, provide us with the light-sensitive emulsions of which this book will largely treat. Trivelli and Sheppard³ describe a series of mercuric iodide emulsions, their sensitiveness and density-giving power being "much inferior to silver bromide." For printing processes on paper, certain salts of iron, copper, thallium, etc., can be used, as also can certain diazo compounds. The outstanding feature of a silver bromide emulsion containing iodide, however, is the fact that by the use of ammonia and the application of heat under controlled conditions, a remarkably extensive range of speed, density-giving power, gradation, and contrast can be obtained, which is repeatable with considerable exactness.

Reduced to its simplest form, the making of a sensitive emul-

4 PHOTOGRAPHIC EMULSION TECHNIQUE

sion has a good deal of resemblance to cooking. Solutions of the reacting salts are weighed out and mixed, one of them containing a little gelatin which acts as a protective colloid and as a means of preventing sedimentation of the halide precipitate. Any amateur cook knows the difficulty of making a good mayonnaise or hollandaise sauce. Some of the tricks of the emulsion-maker are comparable to those of the adept culinary artist, and the sensitometric characteristics of the finished emulsion largely depend on the exact method of mixing and cooking. The mixed emulsion is kept warm for a certain time, during which it is said to "ripen," more gelatin is then dissolved in it, and it is cooled until gelled.

Reference to the equation of the chemical reaction given above will show that soluble nitrate (KNO_3 in this case) is formed along with the silver bromide. Any such nitrates would crystallize out on drying, if allowed to remain in the emulsion when coated on glass or film base, and such by-products must be removed. To effect this, the emulsion is broken up in the jelly stage into small pieces, known as shreds, worms, or noodles, and these are suspended in water until the soluble by-products, together with any excess of ammonia and bromide used in the making, are washed out by diffusion. The washed gel is then dissolved by heat, fresh gelatin is usually added, and the emulsion is again cooked, this time at a higher temperature which is more or less critical, as is also the precise time of the cooking, digestion, or "finishing."

It is the variations in the proportions of ingredients, the exact method of precipitation, the time allowed for ripening, the time of cooking after washing and the temperature employed, and the character of the gelatin, which influence the final characteristics and give us the immense range of modern emulsions. These vary from the very slow silver chloride paper emulsions used for handling in Mazda light, to the exceedingly fast films

that record images in the millionth part of a second. A rough idea of the relative sensitiveness of various types of emulsions is given by Clerc ⁴ as follows —

Ultra-rapid negative emulsions	75,000 to 100,000 *
Positive emulsions, black tones	1,000 to 3,000
Gelatino-bromide papers, warm tones	300 to 1,000
Gelatino-chlorobromide papers	100 to 200
Transparency plates	1 to 25
Gelatino-chloride papers	1 to 5

Silver bromide emulsions made with gelatin are very much higher in sensitiveness than those made with collodion. The digestion of the silver bromide grains or crystals with the gelatin is obviously the prime cause of this difference. Clerc tells us ⁵ that, following from an observation by R. F. Punnett in 1924, S. E. Sheppard found that the differences in sensitive properties are due to the presence in gelatin in varying proportions (from 1 in 200,000 to 1 in 1,000,000) of *sensitizers*, among them being thiosinamin (allyl thiourea), and mustard oil (allyl isothiocyanate). The presence of these sensitizers, occurring naturally in gelatins, and in quantities varying with different makes or different batches of any one brand of gelatin, explains the great variation in quality of any given emulsion made to one formula with different samples of gelatin — a behavior which greatly perplexed the early emulsion makers and for a long time made impossible any assurance of uniformity in their products. Experiments made with gelatins rendered chemically inert, to which have been added known sensitizers, such as allyl thiocarbamide, sodium thiosulphate, etc., have given results qualitatively very similar to those made with untreated “active” gelatin, though the characteristics of active gelatin can not be explained by allyl thiocarbamide alone.⁶ A great deal of research has been conducted in recent years on the chemistry

* This figure must be increased today as the result of recent advances.

6 PHOTOGRAPHIC EMULSION TECHNIQUE

of these sensitizers, and any real advance on present speeds will be due to new discoveries in this field rather than to modifications in ripening, digestion, etc. Elaborate efforts have been made, also, to produce some standard type of gelatin, with little success. As gelatin is an amphoteric colloid, capable of combining with either anions or cations depending on the hydrogen ion concentration of the solvent medium, a good deal of work has been done, by Sheppard and others, with emulsions made with iso-electric gelatin, the pH of which is 4.7. The treatment to which gelatins are subjected by certain manufacturers is kept secret, but as a general practice the choice of a batch from a number of samples by actual experiment is the accepted guide of its suitability for a particular purpose.

As an example of the versatile nature of emulsion grain sensitizing, the suggestion may be quoted of a mononuclear or polynuclear heterocyclic compound containing a hydrogen atom linked to nitrogen but replaceable by silver. The pyrimidines, pyrazols, and purpurines are quoted as examples.

The great majority of speedy emulsions are made with ammonia, which assists in the ripening or crystal growth of the precipitated grains of silver halide and their subsequent sensitivity. In another type of emulsion, however, the suspension in gelatin is "boiled," which means actually that it is heated at a temperature somewhere between 160° F. (70° C.) and a few degrees below boiling point. Such an emulsion is an interesting one to consider at this point, because the absence of ammonia enables us to watch the process with less chemical complications. Trivelli and Smith⁷ outline such a formula. Two solutions are prepared as follows:

Potassium bromide	165 g	Silver nitrate	200 g
Potassium iodide	5 g	Water	2000 cc
Gelatin	65 g	Temperature, 72° C.	
Water	1700 cc		
Temperature, 70° C.			

NATURE OF PHOTOGRAPHIC EMULSIONS 7

In a series of mixings, the silver nitrate solution was added by pouring it through different sized nozzles into the salts solution, the times of precipitation varying from 31 seconds to 85 minutes, 10 seconds. The emulsion was ripened for twenty minutes at 70° C., then cooled quickly to 45° C., when 250 grams of gelatin previously washed in water was added and the whole stirred for twenty minutes at 45° C. After standing overnight in a cold storage room, it was washed and remelted to 42° C. and made up to a weight of 6.3 kilograms by the addition of 100 grams of fresh gelatin soaked in the requisite amount of water. The final pH was 6.54.

The relation between the time of precipitation and the average grain size is interesting, and is shown in the table below:

<i>Emulsion number</i>	<i>Time of precipitation</i>		<i>No. of grains</i> $\times 10^{-9}$ per cm^3	<i>Total surface of grains in cm^2 per cubic centimeter</i>
	<i>Min.</i>	<i>Sec.</i>		
8	0	31	6.85	3053
9	4	22	2.09	1957
10	10	12	0.63	1026
11	19	30	0.28	756
12	42	40	0.17	564
13	54	15	0.09	663
14	85	10	0.04	320

Figure 1 shows the relation between grain size and time taken for precipitation, reproduced from the paper quoted. It was found by Southworth⁸ that there is a quantitative relation between the H and D speed (p. 208) and γ (maximum contrast on complete development), and this was found by Trivelli and Smith to hold good for a number of emulsion series with different times of development.

Let us now examine the making of the emulsion after the initial precipitation of the silver bromide, usually termed the emulsification. As already stated, a great proportion of speedy

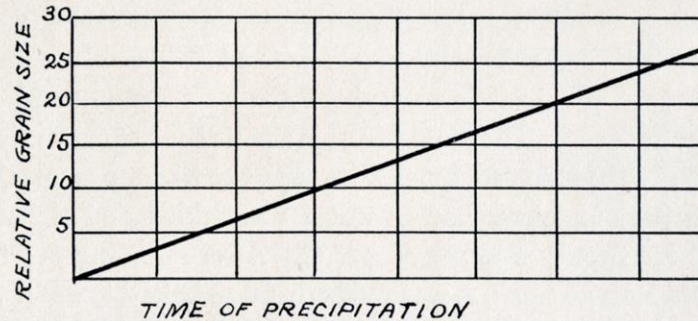


FIG. 1

emulsions are made with ammonia. In many cases the whole of the silver nitrate in the formula is treated with sufficient concentrated ammonia to redissolve the precipitate of silver hydroxide first formed. The temperature of mixing is then usually much lower. The AgBr precipitate formed in emulsification appears as minute shapeless grains under the microscope, but as ripening proceeds they grow in size and a definite crystalline shape is recognized. The crystals continue to increase in size, as time proceeds, owing to the presence of the silver bromide solvents — ammonia and the excess of soluble halide.

Silver bromide, according to von Weimarn's theory, would give a precipitate on mixing the reacting substances, the "grain size" of which would be controlled by the concentration of the reactants. The fact that the precipitation takes place in the presence of a colloid, however, must be taken into consideration, in addition to the excess of AgBr solvents. To obtain uniformity of grain, the emulsion is stirred during precipitation, this tending to reduce the size of the crystals. In some cases of ripening, the crystals are allowed to grow without agitation, especially in those cases where a mixed selection of grain sizes is needed to give photographic latitude, or a long scale of gradation.

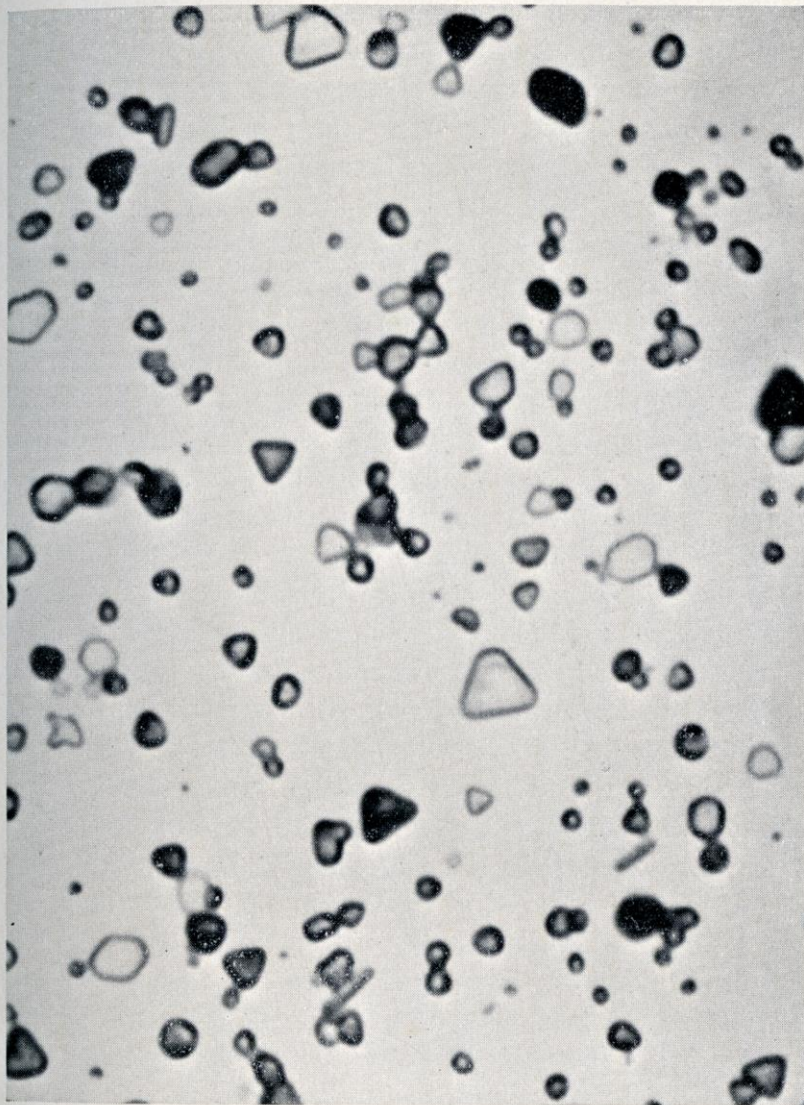


FIG. 2. GRAINS OF A COMMERCIAL PHOTOGRAPHIC EMULSION X 5,000

In the early stages after emulsification the system tends to reduce its surface energy through any colloidal silver bromide becoming transformed into crystalline AgBr. By the so-called Ostwald ripening, the larger crystals grow at the expense of the smaller ones, and the longer the ripening proceeds, the bigger do the crystals or grains become. A certain amount of aggregation eventually takes place, unless stirring is given. A drop of emulsion can be taken on a glass rod, smeared over a clean glass slide, and thinned out with a few drops of hot water. The slide is then sharply shaken free of excess fluid, leaving only a single layer of grains adhering to the surface. The specimen, as soon as dry, can be examined with a twelfth-inch oil-immersion objective, using the concave mirror and small condenser aperture. It will usually be observed that a wide variety of grain sizes is present, appearing as hexagonal plates, triangles, needles and unresolvable particles (see Figs. 2 and 3). All of these are actually octahedra. Dr. Sheppard states that in 122 different emulsions examined at a magnification of 2,500 diameters, only octahedra could be positively identified. The equilateral hexagons which so soon become familiar to anyone examining emulsion grains with the microscope are plates developed in two directions, while needles appear which are developed principally in one direction — all, however, octahedra.

If a few drops of the ripening emulsion be smeared over a strip of glass and looked at by transmitted Mazda light, the color after emulsification will be orange. As ripening proceeds, this turns to yellow, then greenish-blue and then to blue, at which stage the maximum useful ripening will usually have been reached. If ripening be allowed to proceed further, the transmitted light may appear bluish-violet or gray; at this stage the emulsion will have overgone the mark and will probably show fog on development without having gained any advantage in speed. This method of watching the progress of ripening

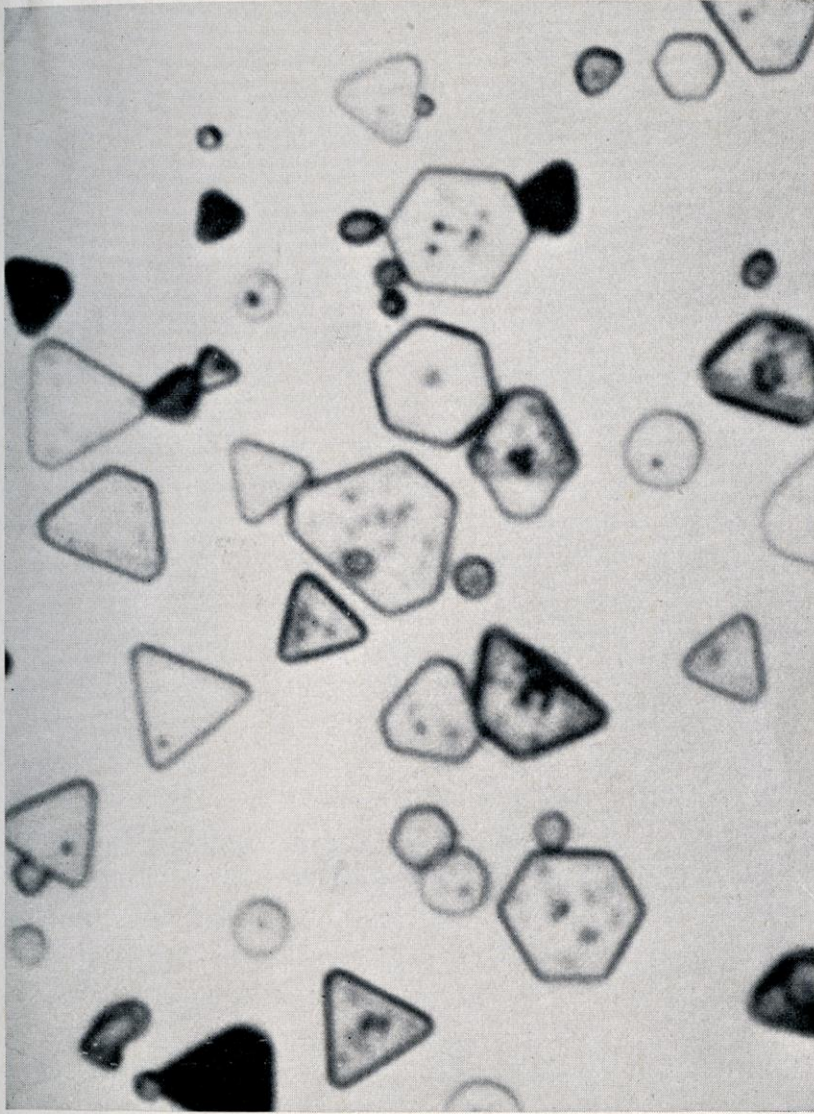


FIG. 3. GRAINS OF A PURE BROMIDE PHOTOGRAPHIC EMULSION X 5,000

was much favored by the old school of emulsion chemists, a trained eye being able to detect with considerable accuracy when the optimum stage had been reached. As the time can vary from twenty minutes or so to three or four hours with an unfortunate change in gelatins, it is a useful check in the factory when new batches come into use, even though they may have been passed as O.K. in the laboratory.

So far we have said little about the iodide in an emulsion. Reference to any formula for a fast emulsion will reveal that a small amount of silver iodide is used. Whether this is formed at the time of emulsification or at a later stage, the iodide appears to take a definite part in the molecular structure of the bromide. Iodine has a greater chemical affinity than bromine for silver, and at whatever stage it is introduced, it will replace it. The term iodo-bromide is frequently used. X-ray crystal measurements of the lattice spacings indicate a complete homogeneity throughout the crystal, but the presence of the iodide ions changes the spacing, making the distance between them larger than in the pure state. This would indicate, according to Friedman,⁹ that a crystal which contains iodide as well as bromide ions exists in a strained condition, the degree of strain being dependent on the concentration of the iodide ions within the crystal. To a slight extent this corresponds to the sensitivity of the resultant grain, for it has been determined that the maximum sensitivity is attained when the concentration of the iodide is approximately four mol per cent of the total halide content. Beyond this concentration the sensitivity falls off again.

The range of diameters of the crystals tells a good deal about the character of the emulsion that is to be. A wide range indicates good gradation and latitude, while if the crystals are all of similar size, a high gamma with early reversal and lack of latitude ordinarily results, except in cases of very slow emul-

sions which have had special treatment. While the grain growth in ripening is almost invariably accompanied by an increase in speed of the finished emulsion, the final sensitivity is determined more by the conditions under which emulsification took place than by the ripening itself, provided always that the final cooking or finishing is carried to completion. The early literature on emulsion making was concerned chiefly with the endeavor to get all the speed before washing. It is now an open secret, since the paper of Carroll and Hubbard was published in the *Bureau of Standards Journal of Research* in 1931, that a great deal of the final sensitivity is obtained in commercial practice by the cooking given to the *washed* emulsion. Trivelli and Smith disclose this fact still further in Communication No. 704 from the Eastman Kodak Laboratories.

The nature of the gelatin undoubtedly plays a very important part, as well as do the concentration of the reacting solutions and the method of pouring and stirring. As an example of the extraordinary effectiveness of emulsifying conditions, one may take a formula, built on lines originally published by J. M. Eder, where the silver nitrate is merely wet with water, redissolved with ammonia, and in this very concentrated condition is literally "flopped" wholesale on to the salts solution in the jar. This, of course, gives an instantaneous precipitation, the grains being of a very uniform size. No ripening time whatever is allowed, the bulk gelatin being added immediately and the emulsion set in ice water as soon as it is dissolved. Such an emulsion yields a film of very high gamma but of poor latitude, specially suited to copying black and white work. It will thus be gathered that the emulsion chemist must find out for any emulsion formula the optimum time of ripening and the necessary physical conditions to obtain the results he wants, as also the exact method of emulsification, in addition to selecting the most suitable brands of gelatin.

Let us assume now that an emulsion has been ripened and that sufficient extra gelatin has been added to give it the necessary viscosity for coating — say a total of eight or nine per cent of the volume. This viscosity is of course arranged to suit the type of plate, film or paper, and the particular coating machine and climatic conditions. The soluble by-products together with any excess of ammonia and the excess alkali halides, are next removed by washing. While this is ordinarily done in the manner described in detail in Chapter III, other methods have been suggested, such as pouring the emulsion in a fine stream into a large bulk of alcohol, thereby coagulating or precipitating the gelatino-bromide, the water with its soluble salts being taken up by the spirit. Many variations of the spirit washing method were described in the early literature, especially in the *British Journal of Photography*, towards the end of the last century.

The washed emulsion, then, is a dispersion of silver halide grains in more or less pure gelatin. The gelatin nevertheless contains sufficient sensitizers — or they have been already adsorbed to the silver bromide crystals — to insure that when the emulsion is remelted and heated the maximum sensitivity is obtained. That some sensitization has been effected within the grain in the case of mixed-grained emulsions has been shown by the fact that while after exposure the smaller grains can be rendered undevelopable (the latent image destroyed) by treatment with chromic acid, some of the larger grains still remain developable. The final cooking, when the speed of the washed emulsion can be increased many hundreds or even thousands of times in the course of thirty minutes or so, is known as digestion or finishing, and is fully dealt with in Chapter IV.

Owing to the lack of emulsion-making literature, particular interest attaches to the paper by Trivelli and Smith¹⁰ in which are described experiments to determine the influence of grain

size on the final digestion. These experiments indicated two things; (a) the H and D speed of the smaller-grain emulsions increased to a greater extent than that of the large-grain emulsions; (b) the gamma of the smaller-grain emulsions increased less than that of the larger-grain emulsions. As an example of (a), the figures below are quoted from the paper of these authors:

Average grain size in μ^2	0.16	0.54	2.93
<i>Time of finishing at 60° C. in minutes</i>	<i>Increase in speed</i>		
10	3.4	3.8	0.8
20	4.6	5.0	0.9
30	5.2	4.4	0.9
40	5.9	4.7	1.0

Average grain size in μ^2	0.16	0.54	2.93
<i>Time of finishing at 60° C. in minutes</i>	<i>Increase in gamma</i>		
10	1.4	1.6	2.5
20	1.5	1.7	2.9
30	1.5	1.9	3.2
40	1.5	1.9	3.2

Admitting that grain size need not be the deciding factor in the speed of an emulsion, it has been established that within experimental limits there is a direct proportionality between the average grain size and the H and D speed in certain emulsion series. On the other hand, as the gamma of very fine-grained emulsions does not increase as much on final digestion as it does in the case of coarser-grained ones, it is usual practice to secure the high contrast (where desired) of a slow fine-grained emulsion in the mixing and ripening rather than to trust to the digestion after washing. Speed being due largely to the sen-

sitizing of the silver halide by the gelatin, it is obviously more difficult for the gelatin to function in the case of *fine* grains, which have a very large surface as compared to the coarse grains. As an example in the increase in surface area of a grain with decrease in diameter, the illustration may be given of a cube of 1 cm side, which has a free surface of 6 sq. cm. If divided up into a corresponding number of small cubes each of 0.01 thousandth of a millimeter side, the free surface of the 6 sq. cm would be expanded to an aggregate of 60,000,000 sq. cm.

Reference may be made here to the effect of very small quantities of sodium sulphite in emulsions. If this substance be introduced in quantity sufficient to reduce a few tenths of one per cent of the silver bromide present, and the emulsion be then digested, it can act as a powerful sensitizer, approaching in large measure the effect of the natural sensitizers in gelatin. As stated by Carroll and Hubbard,¹¹ the sensitivity nuclei formed are of metallic silver, in amounts similar to that of the silver sulphide nuclei of normal emulsions. The rate of change of sensitivity increases with increasing alkalinity, and decreases with increasing bromide-ion concentration. The rate of after-ripening with sulphite is less affected by hydrogen ion concentration than the corresponding process in active gelatin. The authors state that while many of their emulsions sensitized with sulphite were of "commercial quality," none were equal to the best obtainable by standard methods from the same type formulas.

After the emulsion has been coated on its support, a certain amount of after-ripening or ageing can go on, especially if the ripening after emulsification has not been carried to, or near to, an optimum point, or if the finishing was not carried to finality. This gradual rise in speed or gamma in a coated plate on keeping is not to be confounded with the after-ripening

which Carroll and Hubbard define as "the increase in sensitivity of photographic emulsions after washing," which we have seen depends on the effect of heat treatment upon the initially ripened grains.

The ageing of plates and films may be regarded as a continuation of digestion in the dry state and at storage temperature, but for our purpose it should be regarded more as deterioration. A coated product, after keeping for a short time to get into complete equilibrium and for the hardening agent to complete its work, should maintain the state in which it is put out for two to three years, and much longer in the case of slow materials. On the other hand, there may be a tendency in the case of films for the gradual lowering of pH, due to acid liberation, when speed will be lost. This is a matter to which due attention must be paid in commercial film manufacture. As an instance of the excellent keeping of glass plates, the case may be quoted of star drift measurements at Oxford Observatory, England, where special rapid plates were exposed in an astronomical camera on a group of stars, and without development were stored for fourteen years, and then given a second exposure at the completion of the orbit. The displacement between the two images, one having been latent for fourteen years before development, was the measure of the drift.

When light is absorbed by a grain of silver iodo-bromide, the silver halide molecule becomes dissociated, and atomic silver and free halogen are formed, the halogen being absorbed by the acceptors in the surrounding gelatin. The new system can be described as a crystal of silver iodo-bromide upon which atomic silver is adsorbed. Such a system is easily reduced to metallic silver by the action of the developer, as originally established by Carey Lea. That the reduction starts from the sensitive nuclei was shown in 1922 by the brilliant photomicrographic researches of The Svedberg.

The metallic silver grains formed from the exposed silver halide by reduction during development have been regarded as tiny coke-like masses, which link up to form aggregates or larger "grains," but it has been shown by recent work with the electron microscope that the grain formation is actually ribbon-like in character. Photomicrographic work done in the ordinary way up to magnifications of $\times 2000$ and upwards (diam-



FIG. 4

eters) has never revealed, nor indicated, such a formation. But with the immensely greater magnification of $\times 50,000$, possible with the electron microscope, definite results have been secured which may necessitate reconsideration of some of our present ideas. The image grain has now been shown (Fig. 4) to consist of a ribbon of silver crumpled up like a string, which would appear to occupy a part only of the total area of what we have regarded as the *grain* and to possess light transmitting properties rather than being completely opaque. It is more than likely that subsequent studies along these lines will show the structure to vary as regards its nonopacity with different condi-

tions of emulsification, and thereby be responsible to some extent for characteristic variations.

It is beyond the scope of this book to deal with the subject of the latent image and the theory of development, but it should be emphasized that one reason why sensitive silver emulsions have made modern photography possible and of such immense value to scientific research, is that over a long range of light intensities, depending on the individual emulsion, equal increases in exposure result in equal increases in opacity of the developed image, or equal increments of "developability."

Equal effective exposures produce equal densities under controlled development (Bunsen and Roscoe reciprocity law), except for a correction indicated by Schwarzschild which makes it necessary to substitute for the exposure $I \times T$ (intensity multiplied by time) $I \times T^p$, p being the Schwarzschild factor. An example is given by Strong,¹² showing to what extent the Bunsen and Roscoe law fails in the case of motion picture positive film. For a range of illumination intensities from 1 to 33,000, p varies from 0.68 to 1.00, the maximum intensity being 131 lumens per square meter and the exposure time varying between 18.2 hours and 2.5×10^{-4} second.

The covering power and maximum density of an emulsion depend to some extent upon the size of the reduced silver grains, their aggregation, and their number per unit area, the ratio of gelatin to silver having some effect where density measurements are made by specular light. Clerc states¹³ that an optical density of 1 (transmission ten per cent) on a photographic negative, corresponds to a mass of silver of about ten milligrams per square decimeter, a mass which is variable with the grain size, conditions of development, and the wavelength of the radiations used. Trivelli and Smith showed¹⁴ that the decrease in gamma of an emulsion is proportional to the square root of the total number of grains. They state that this de-

crease is considerably greater than the changes observed in the *resolving power* by diluting the emulsion. For recording purposes, a good black which will give sufficient differentiation in printing or on projection must be combined with high resolution, and the latter must therefore depend largely on suitable emulsion characteristics rather than on thin coating. In fine-grain emulsions, however, Trivelli and Smith find that the resolving power increases exponentially as the grain size is diminished arithmetically.

Much of the foregoing has applied to "rapid" emulsions of silver iodo-bromide having H and D speeds ranging from 25 to 2000 or more. In materials for printing, lantern-slide emulsions, and copying, speed is of little consequence. Where extra-fine grain, high resolution and negligible fog are the chief desiderata, physical treatment rather than chemical is involved, and in chapters dealing with such emulsions it will be seen that the general technique of making is considerably modified.

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CHAPTER II

MATERIALS FOR EMULSION MAKING

Gelatin — Chemicals and Their Choice — Analyses and Tests — Storage
— Methods of Handling Bulk Materials

GELATIN is the material which presents the most problems to the emulsion chemist. Its physical and chemical properties can be tested in the laboratory, but the physical characteristics are apt to change according to the treatment it undergoes, and the chemical properties from an emulsion-making standpoint depend to an important extent on certain constituents present only in extremely minute quantities. Bogue states¹ that the gelatin solution used in an emulsion must be so made that the dried film will have just the right porosity to electrolytes, for in all stages of development where chemicals are used it is necessary that they penetrate and impregnate the gelatin layer with considerable ease, but no trace of the precipitated silver must be permitted to escape. Gelatin acts both as a protective colloid and a vehicle for the silver haloids, and it is in fact quite astonishing what a mass of silver haloid can be suspended in a very weak solution of gelatin with comparatively slight sedimentation.

The best gelatin for emulsion-making purposes is probably that extracted from calves' hides, but other hides and other parts of the animal are used, and bones also. Hides having a high fat content are not suitable for emulsion gelatin, according to Huzii,² as it causes spots on the plates. If the temperature in extracting the gelatin is too high, the product will have high light sensitivity and fog-giving properties; increase in the number of extractions has similar effects.

The preparation of the gelatin involves a number of operations. The raw materials are steeped in lime water, after having been thoroughly washed free of dirt and blood. The liming process dissolves out the albuminous and mucinous constituents, and, as it is a process of alkaline hydrolysis, caustic alkali is sometimes employed. The alkali is later neutralized and a process of digestion or boiling given, followed by concentration of the liquor, bleaching, washing, etc. The final jelly is cut into sheets and dried on strings or wire nets, and here a certain amount of bacterial contamination can be contracted. Leaf gelatin is sold in the form of thin sheets, of which in the photographic quality 100 to 110 go to the pound. It may be cut into thicker sheets which are ground to powder when dry, or turned into flakes which are sometimes sold as such. The ground gelatin when sieved gives a powder of about 50 per inch mesh. Such powder is liable to contain traces of iron. Photographic gelatin, which may be looked upon as gluten and a mixture of gluten and chondromucoid, is the purest form made, being superior in quality to culinary gelatin.

A good gelatin should give a clear and nearly neutral solution. The moisture content should not be more than twenty per cent and lower in the case of "soft" gelatins. There are roughly three classes of photographic gelatins, hard, medium and soft, which can be differentiated by their setting and melting points and the quantity of water they will absorb. The ash content of a good gelatin should not exceed two per cent. Bases and heavy metals should not be present in more than traces; these may be sodium, calcium, zinc, iron, copper, arsenic, nickel. Phosphates, sulphates, sulphites, chlorides, borates and sulphur dioxide may also be present.

It is interesting to note that as early as 1847 Niépce employed gelatin as a vehicle for coating silver iodide on glass, though this was soon dropped owing to the effect of the acid

nature of the silver bath. Eight years previously, Mungo Ponton had rendered paper sensitive to light with potassium dichromate, and later Becquerel showed this sensitivity to be due to the *size* in the paper. It was Dr. R. L. Maddox who, in 1871, first employed gelatin as a vehicle for silver bromide and so prepared the first emulsion. Its use gave an entirely new measure of speed, but it at the same time introduced a great many perplexing phenomena, some of which are still not fully understood.

Dr. S. E. Sheppard quotes in his monograph on the theory of photography, "Gelatin," a statement by V. B. Storr³ in the *Second Annual Report of the Society of Chemical Industry* on the progress of applied chemistry, as follows: "The physical properties are a very insufficient guide to the suitability of gelatin for making photographic emulsions. There are certain chemical differences between different types of gelatin and even between different batches of the same type which are more effective in determining speed, freedom from fog, and such qualities. . . . It is very possible, if not probable, that they (chemical differences) are due to the presence or absence of very small quantities of specific substances rather than to variations in the proportions of the main constituents of the gelatin."

This statement tells a good deal of the story of gelatin, and every emulsion chemist will add to it that the only satisfactory way of testing a new sample is to make with it a semi-works-size lot of the particular emulsion for which it is to be used. It is a common occurrence, for example, for a sample which has been turned down by one maker to be accepted as excellent by another. Where results are to be repeated over long periods, or where works-batches of emulsion are being made, it is sound practice to use a blend of two or three different lots or even makes, taking care that only one of these is allowed to run out at one time, so that when a new batch of gelatin is worked in,

only a proportion of the total amount used for each making is changed.

The chemical test of most importance in selecting gelatin is for silver reduction. A one or two per cent solution of the sample is made up with distilled water, and to a measured volume is added an equal volume of ten per cent silver nitrate solution, to which has been added just sufficient concentrated ammonia to redissolve the precipitate of silver hydroxide first formed. The mixture is well stirred and is then left in the dark for a fixed time, along with a similar control test of a gelatin of known good quality. Any darkening or formation of a precipitate will give a good indication of the quality of the sample. A good gelatin will contain a relatively small proportion of non-glues. According to Stelling,⁴ the non-glue extracted from gelatin by alcoholic precipitation of the glue is 3.39 per cent, 5.73 per cent from hide glues, and 10 to 16 per cent from bone glues. Arsenic has some effect on speed and fog production, and has been found to occur in eight out of twelve samples,⁵ in the proportion of 0.0005 to 0.003 per cent. Copper, zinc, tin and lead may be found by the usual methods. The most important impurities are probably the sulphur compounds dealt with elsewhere. The presence of sulphur dioxide is undesirable, especially if the sample is to be used for highly color-sensitive emulsions or for the making of light filters. Where leaf gelatin is to be used for the latter purpose, it can be washed in several changes of water before use, the leaves being kept well separated, when soluble impurities will be removed.

Viscosity can be measured in a number of ways. A one per cent solution may be tested with an Engler or Ostwald viscosimeter, at a temperature of 120° F. Running the solution through a water-jacketed pipette and comparing the time taken with that of plain water is another and cruder test, but one which will give useful practical information. Thermal hys-

teresis or hydrolysis may upset physical tests, for it must be remembered that previous treatment such as heating up rapidly and cooling, gelling and remelting and so on, may alter the behavior of a gelatin solution. The viscosity of most gelatins can be very largely controlled in an emulsion by modification of the concentration, by the addition of alcohol or acetone, or by the addition of chrome alum, formalin or sodium sulphate.

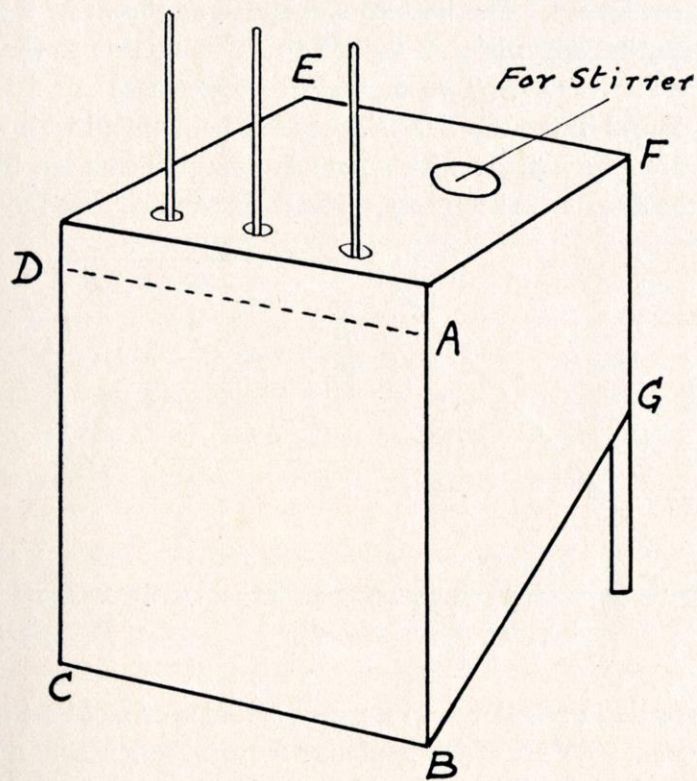


FIG. 5

The melting and setting points of a sample are of some importance. Emulsion gelatins should have a melting point somewhere between 70° and 78° F. (22° and 25° C.) and a setting point of 79° to 86° F. (26° to 30° C.). R. Child Bayley's

method of estimating melting point was to cast small discs of gelatin upon a flat metal surface, which is afterwards placed in a *vertical* position and heated. At the temperature of the melting point, the discs begin to slide downwards. The apparatus takes the form shown in Fig. 5. This is a copper tank having a plain front say twelve by eighteen inches in size, with a smaller back about nine by twelve inches, the depth *AF* being about ten inches. The bottom is inclined as shown in the diagram, so that when heat is applied to *BG* none gets to the testing surface *ABCD*. Two or three thermometers are fitted in corks placed in the top *ADEF*, the tank being filled with water and gradually warmed with an alcohol lamp or Bunsen burner after the discs have been cast. The discs can be made by pour-

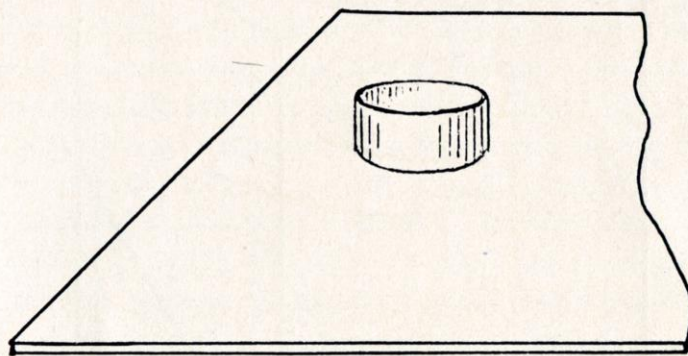


FIG. 6

ing the gelatin solution into a paper cylinder or mold set up on the surface *ABCD*, which is placed first in the horizontal position (see Fig. 6). Tests should be made with solutions of some uniform strength. E. J. Wall recommends ten per cent. The gelatin solution may be introduced into the molds with a pipette, each one being cast of the same height, about one-half inch. The tank should then be left in the cold for eight hours until the gel is thoroughly set and in equilibrium. The tank is

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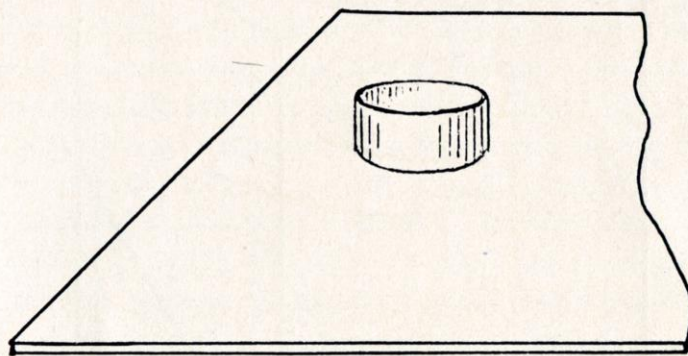


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then set in the upright position, the paper cylinders cut round with a sharp penknife and removed, and the tank filled with water. A small motor stirrer is advisable to keep the whole front surface uniformly heated. As soon as the melting point has been reached, the little discs will begin to slide down the face of the tank, and the average temperature of all of them will give the melting point desired.

Another method, used a good deal by the author, is to introduce the gelatin solution into four little glass tubes one and one-quarter or one and one-half inches long, and about three-sixteenths-inch bore. These are set and kept cold, at about 45° F. for four hours, and are then tied around the bulb of an accurately graduated thermometer. The bulb and tubes are then suspended in a beaker of thin petroleum oil of about 0.90 specific gravity, the beaker standing in an outer water bath. A small mechanical stirrer keeps the oil in motion. The water jacket is heated, and as the oil approaches the melting point of the gelatin, the gelatin slips out of the glass tubes and drops to the bottom of the beaker. An average reading of the four tubes will then give a fairly reliable figure for the melting point.

The setting point, which is on the average eight to ten degrees Fahrenheit higher than the melting point, can be ascertained in various ways. Sheppard⁶ describes one method which is stated to give results of the accuracy commonly required in emulsion making, which is as follows: Equal amounts of the solutions to be tested are placed in similar test tubes of one-inch diameter. These are then cooled in ice water and are examined at definite intervals, until the approach of solidification is indicated by the fact that the solution is hardly disturbed when the tube is tilted. When this stage is reached, the tubes are inverted at frequent short intervals. When the meniscus of the inverted sample no longer sags, a thermometer is thrust into the jelly

and the stationary temperature is taken as the setting point. The rate of setting is, of course, of considerable importance when emulsions are to be coated on any kind of machine in the factory. Generally speaking, it may be said that the rate of setting is reasonably gauged by the viscosity, or the jelly strength.⁷ While the rate of setting and the setting point can be controlled to a large extent by additions of hardeners (alum, formalin, etc.) or alternatively by softeners (glycerin, etc.), if a gelatin can be selected which resembles previous stock without alteration of the additions, it is far better. The use of chrome alum, for example, is cumulative, and plates or films coated with an emulsion containing it will go on hardening for several months, during all of which time the rate of penetration of the developer will be progressively retarded, with a consequent alteration in the apparent speed unless carefully checked.

It is very desirable in all tests of the physical characteristics of gelatins to submit the sample to the same initial treatment. Thus any change in pH will be responsible for wide variations in the swelling capacity. The ions of many salts have a profound effect on physical properties. As an example of laboratory practice, in making a five per cent solution, 5 grams should be weighed out and placed in small pieces in 90 cc of distilled water (or tap water if the test demands), and allowed to swell for one hour at room temperature, 70° F. The water is then warmed, the gelatin dissolved by stirring, and the volume brought up to 100 cc. The temperature should not be allowed to exceed 160° F. It should then be stood on the bench and allowed to cool until it attains the temperature that is required for the test, for which a suitable temperature would be 105° F.

An example of a commercial test is tabulated on the next page.

MATERIALS FOR EMULSION MAKING 29

GELATIN TEST. Lot No. 117.

Grease	None
Clarity	Complete
Engler viscosity at 10%, temp. 35° C.	3.3
Setting point of 10% solution	27.8° C.
Melting point of 10% solution, after two hours.....	31.9° C.
Reduction by ammonia-silver nitrate	None
Copper, lead, zinc	None
Iron salts	Traces
pH	5.6
No. of cc of 5% chrome alum required to precipitate 10 cc of a 10% solution at 50° C.	5.9

For more detailed information on gelatin, the reader is referred to Dr. S. E. Sheppard's monograph "Gelatin," Vol. 1; Kissling's "Leim und Gelatin" (Stuttgart, 1923); and the textbooks of Alexander, Bogue, and others.

The brands of gelatin largely used in emulsion making are Nelson's No. 2 and Nelson's X-opaque and S. E. emulsion leaf, (made at Warwick, England), Simeon's Winterthur (Swiss), Heinrich's and D.G.F. (German), Bertrand's (France), and last, but not least, the excellent products of the Atlantic Gelatin Co. and American Agricultural Co. Most makers are generous in the extreme with regard to supplying samples, but it is a useful guide to them when ordering to specify the approximate viscosity and hardness desired, if possible to send samples of those brands in use, and to state the type of emulsion for which the gelatin is wanted — fast negative, slow positive, bromide or chloride paper, and so on. Prices average about 85 cents to \$1.25 per pound, and as an example of likely quantities for commercial work on a moderate scale, about twenty-five to thirty pounds may be estimated for each day's run of 3,000 feet of sensitized material forty-two inches wide. Gelatin will keep almost indefinitely if stored in a cool and dry place, and it is the experience of many firms that if kept for

six months before use it gives the best results. As already stated, bulk gelatins are best made up of mixtures of two or three batches or makes, which are arranged to run out at different times. A couple of weeks should be allowed to make a thorough test of a new sample. In making the test, a word of caution may be given. In packaging leaf gelatin it is the manufacturers' usual practice to draw from two or three bins, so that a one-pound packet may contain three or more different varieties. If fifty grams are required from a pound packet, a cross section of sufficient thickness should be cut on the cutter so that a piece of each sheet is included in the test solution.

The reader may wonder why gelatin remains the only colloid which is successfully employed as a vehicle for sensitive silver salts. Its sensitizing properties are sufficient reason, but its vehicular power, porosity and protective powers combine to make it unique. Collodion is still used in process work, and for special types of emulsion of a slow speed. Silver halides can be precipitated in a solution of pyroxylin in alcohol-ether, and collodio-bromide and collodio-chloride papers have long been in commercial use. They possess one advantage, that if coated on a base first coated with gelatin, the developed image in collodion can be removed or stripped off the support by treating the print with hot water, which dissolves the gelatin interleaf but does not affect the collodion. An example of this is the Defender Chromatone bromide paper. The image, after toning, can be floated off the support and mounted in layers for the production of a three-color print. Stripping papers can be similarly made for a variety of purposes, although it is a doubtful point whether a coating of hardened gelatin emulsion on top of a gum dammar or wax coating of the support does not yield a better material.

We have seen in Chapter I how excessively small need be the proportions of ingredients or impurities in gelatin to be

responsible for important changes in emulsion quality. It is therefore easy to understand that all chemicals used in emulsion making should be of a high order of purity. There are three types of chemicals generally available. One is the standard type sold for amateur and professional photography. Another is the so-called chemically pure or C.P. variety, and a third type is sold for the laboratory for more exact work, described by the term analytical reagent or A.R. For emulsion making in small quantities, A.R. chemicals are worth the extra cost. At least silver nitrate and ammonium bromide should be A.R. quality. In general, other chemicals may be of the C.P. type. In all formulas given in the following pages, water may be taken to mean distilled water unless otherwise stated. Emulsions are usually washed to best advantage in tap water, or supplies from artesian wells.

Of the ordinary emulsion-making ingredients, ammonium bromide is one of the most important. For extreme speed emulsions this should not contain more than 0.2 per cent of chloride. The finest quality is probably made by combining purified bromine, free from chlorine or hydrobromic acid, with pure ammonia liquor. Less pure samples can be improved by re-crystallization. The chloride content can be checked by boiling a weighed sample with concentrated pure nitric acid, driving out the bromine, and titrating the residue with centinormal silver nitrate solution.

Silver nitrate is made by dissolving silver metal free from copper and lead in nitric acid. The carefully re-crystallized product is usually sold at a price calculated on the ruling price of silver at the time of order. It must be free from nitrite. Its formula is AgNO_3 ; that is, it is a salt without water of crystallization; molecular weight 170. For convenience, it may be kept in the form of a concentrated solution, such as 2N or $2\frac{1}{2}$ N, in stone jars. In the following text, however, many

formulas will be found in which the silver nitrate is "wetted" with a small quantity only of water in order to convert it into a highly concentrated solution of the ammonio-nitrate. Here the dry salt will in most cases be found more convenient.

There is much to be said in favor of keeping chemical stocks in liquid form. It is probably more accurate and definitely more convenient. In the case of silver nitrate, if a 2N solution containing 340 grams per liter is made up, the ammonium bromide may conveniently be made up also as 2N, having 196 grams per liter. Equal quantities then react completely. On the other hand, such a reagent as ammonium bromide, which is used in slight excess of the equivalent weight of silver, may be found more convenient to handle in the form of a ten per cent solution.

Ammonia must be free from iron and pyridine compounds. There is an advantage in breaking down the concentrated ammonia to 0.920 specific gravity, as at this strength each cubic centimeter will almost exactly re-dissolve one gram of silver nitrate or be equivalent to one gram of AgNO_3 . It will be found a great convenience to have it delivered in this form, although the gravity must be checked from time to time. Ammonium and potassium iodides are best made up in the form of solutions and kept in the dark when not in use. A discoloration on keeping, due to the liberation of some free iodine, need not be feared. Indeed, some emulsion makers think that the solution in this form is preferable. Chrome alum should be selected free from contamination by small orange crystals of dichromate, and should be made up with water not above 100°F ., as otherwise it may decompose and lose its hardening properties. It should not be neutralized. Chrome alum is most usually handled in the form of a five or ten per cent solution, which should be re-filtered if at any time, on keeping, it shows a deposit.

It is assumed that a reasonably accurate balance or pair of scales is available, and a larger balance where works-scale quantities are to be weighed. A balance sensitive to one or two milligrams is needed, since in many emulsion formulas the reacting compounds are used in proportions closely approximating to their combining weights. The type of chemical balance which

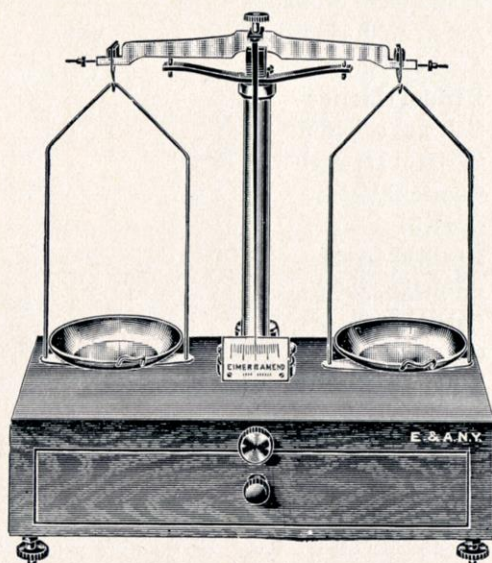


FIG. 7

depends on a moving weight sliding over a scaled bar is not recommended, but a balance of the laboratory type shown in Fig. 7. A set of weights ranging from one gram to five hundred grams with fractions to ten milligrams is suggested.

The following is a list of the chief chemicals which will be needed in the course of the work described in this book:

- Acetone
- Acid, acetic, glacial
- Acid, citric
- Acid, hydrobromic
- Acid, hydrochloric

Acid, nitric
Acid, phosphoric
Acid, sulphuric
Alcohol, denatured, photographic quality
Alcohol, pure
Alum, chrome
Ammonia, concentrated
Ammonium bromide
Ammonium chloride
Ammonium iodide
Barium chloride
Calcium chloride
Carbitol acetate
Cupric chloride
Dextrin
Distilled water
Formalin, 40%
Gelatins, various
Glycerin
Litmus paper
Methyl alcohol
pH indicators
Nessler reagent
Phenol crystals
Phenolphthalein
Potassium bromide
Potassium chloride
Potassium citrate
Potassium dichromate
Potassium iodide
Potassium thiocyanate
Rochelle salt (sodium potassium tartrate)
Sodium chloride
Sodium citrate
Sodium oleate (glycerin substitute)

It is assumed that the usual photographic chemicals are available. Calcium chloride or sulphuric acid will be required for the desiccator.

A word may be said here about alcohol. Denatured spirit to be used in emulsions must be free from mineral oil, aldehydes, pyridine or any coloring matter. A special type of industrial spirit is made for the photographic industry which consists of ethyl alcohol (C_2H_5OH), with a small percentage of wood spirit or methyl alcohol (CH_3OH). This, however, can only be obtained with a permit. A form of denatured alcohol containing about one per cent of gasoline which has been used by the author with most types of emulsion with success, can be obtained without a permit in any quantity. This is Synasol, supplied by Carbide and Carbon Chemicals Corporation, 30 E. 42nd Street, New York City. Where emulsions are to be used for commercial purposes it would not be recommended, but for experimental work it may be found a great convenience. Where only small quantities of spirit are likely to be used for laboratory scale experiments and cost is of no object, the reader is advised to use pure grain alcohol or ninety per cent alcohol, both of which are available in most laboratories. In works practice, a permit will be required for the necessary amount of industrial spirit, which will run into considerable quantities. Spirit is used in commercial emulsions in proportions varying from five to ten per cent of the total volume. In factory routine, frequent checking up of the spirit is necessary to look out for the presence of aldehydes or other deleterious impurities.

While a still for the preparation of sufficient quantities of pure water is an essential on any works-scale production, what is more important in selecting a site for an emulsion laboratory is to determine whether or not the available water supply is suited to the work.

Chapter References

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36 PHOTOGRAPHIC EMULSION TECHNIQUE

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CHAPTER III

LABORATORY EQUIPMENT

Layout for Experimental Work — Commercial Production and Its Requirements — Ventilation — Safelights — Digesting Apparatus — Thermostatic Control — Washing and Filtering of Emulsions — Making up — Cold Storage

THE accommodation required for emulsion making depends primarily on the quantities involved and type or types of product to be made. As already hinted, one of the first things to be ascertained in contemplating commercial production is the suitability of the water supply or the provision of good water, and freedom from atmospheric contamination. While modern air-conditioning plants make it possible to work in towns and cities, a new plant is generally started in a vicinity where the air is clean and fresh and space is plentiful.

We shall endeavor in this chapter to discuss plant and apparatus both for the experimentalist and for the production of commercial quantities. In many instances, of course, the larger plant is a multiplication of the smaller unit. But where the coating is to be done by any type of machine, conditions are necessarily very different from experimental work where the coating is by hand. The laboratory type of work will be dealt with first, but it will be understood that much of what is said applies to both cases.

While small quantities of emulsion of excellent quality can be made in the laboratory, even in speedy varieties, the emulsion maker must have the right tools to work with, light-tight accommodation, reasonably good ventilation, an ample water supply, and above all, a room free from dust for coating, where heat up to 70° or 75° F. can be more or less controlled. Very

small scale work can be done in one room, used alternatively for mixing, washing, coating and testing. In many instances of experimental work this is the only condition under which it can be carried on. The ideal accommodation for small-scale work, however, is to have at least four rooms or subdivisions of a large room, where (*a*) the solutions can be weighed out and prepared, (*b*) the emulsification, ripening, washing and digesting can be carried out, (*c*) the finished emulsion can be coated and dried, and (*d*) the final product can be tested or used for photographic work. The latter is obviously the average photographer's darkroom.

The coating and drying room should be as free from dust as possible, with sufficient and suitable ventilation which involves no light leaks. Cleanliness and order are above all things to be desired, the utmost care being taken to keep all graduates, crocks, stirring rods, beakers, dishes, thermometers, etc. scrupulously clean. Cupboards are better than shelves for storing chemicals and apparatus, bottles and glassware being first class dust catchers and requiring frequent rinsing and wiping with a clean damp cloth.

Any room to be used for coating and drying sensitive material must be thoroughly light-tight, this usually involving rather more investigation than would suffice in ordinary darkroom work. By shutting oneself in the room in complete "darkness" for ten or fifteen minutes, it is often astonishing to find how much stray light there is in a room previously thought to be absolutely dark. Black or dark brown paper and paste or glue is generally a sufficient remedy, or the filling up of cracks with mortar or plaster of Paris. A strip of felt or rubber beading along the bottom of doors is often a help, or a wooden lath screwed to the floor to cover the clearance space. Benches about three feet high are more convenient than tables, as practically all work must be done standing and not sitting. This does not

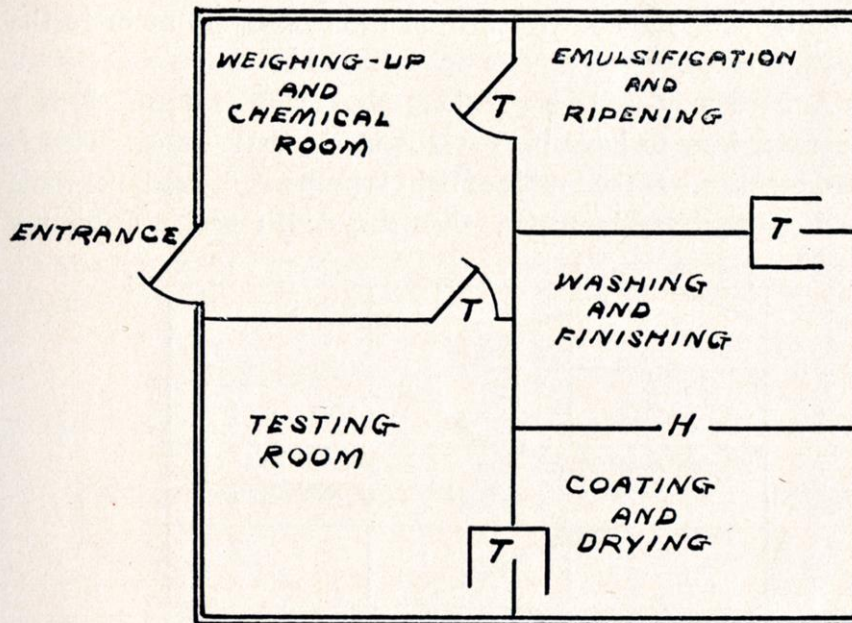


FIG. 8

apply to benches with sinks for washing jars and crocks, where a more convenient height is two feet to two feet, three inches. Sinks should be of ample size, and if of porcelain or enamelled iron and not of wood, wooden slats should be placed over the bottom to prevent breakage.

A small layout is shown in Fig. 8, in diagrammatic form. The general idea, as is often suggested for commercial laboratories, is that the work should take place in a cycle, one operation following another in the ordinary sequence, so that chemicals and solutions are prepared at one end, and the testing of the finished product can be carried out at the other. It is a great convenience to have a light trap between the coating room and the emulsifying room, as shown at *T* in Fig. 8, as one can then go freely from "light" to "dark" at will. If two people are doing the work, a small hatch *H* with sliding panel is useful for han-

dling crocks, solutions, etc., from the making-up room to the coating room.

A word may well be said here about illumination. It is a common idea to have black walls in the darkrooms. This is bad practice. If the source of light is properly filtered, the walls and ceilings may be *white*, when they will reflect a maximum

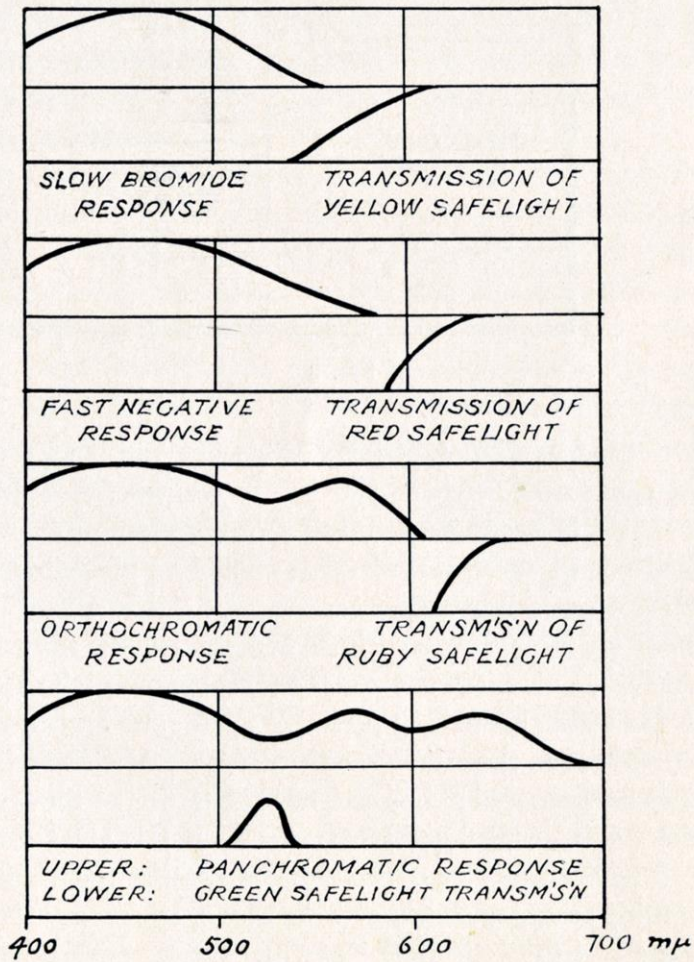


FIG. 9

amount of diffused light from all parts and greatly increase comfort in working. Inverted ceiling lamps throwing the light upwards so that no direct rays fall on the bench or table are the best to use for general illumination. The ordinary vertical type of lamp will be needed on the benches themselves. Electric torches provided with a piece of "safe" gelatin or glass fitted in the top should be provided for reading thermometers in the darkroom.

<i>Type of emulsion</i>	<i>Color of safelight</i>	<i>Type</i>
Chloride and chlorobromide	Yellow	Wratten OO Agfa 105
Bromide paper or transparency . . .	Orange	Wratten O or OA Agfa 104
Non-color-sensitized	Red or yellow-green	Wratten Series 1 or Series VIa
Orthochromatic	Deep red	Wratten Series 2 or Agfa 107
Panchromatic	Narrow-cut green	Wratten Series 3 or Agfa 108
Infrared	Same as for panchromatic	

The spectral transmission of these various types of safelight is shown in Fig. 9, with the average spectral response of types of emulsions for which they are recommended shown immediately above them. Ground-glass bulbs are to be preferred to plain glass as they diffuse the light better, unless the safelight glasses themselves are of the diffusing type. Ten-watt bulbs are obtainable from most photographic dealers and should be used in the bench lamps.

As white light must also be provided in all rooms, it is a good plan to place the switches for them high up at the side of the doors, so that a physical effort must be made to reach them. This simple arrangement almost entirely prevents turning on the white light by accident. In any works operations the need

for proper light traps between darkrooms is imperative, and automatic switches are usually provided for making it impossible for anyone to turn on the white light when the safelight is being used. The white lights in the emulsion and coating rooms should be of low candle power in order to keep the eyesight for dark operations. It is customary in modern coating and cutting rooms for operatives to spend a few minutes in a preparatory room of very low illumination before starting work, and to rest there for a short time after work to accustom the eyes to the change of level.

As regards apparatus, we shall again consider the experimental requirements first, discussing the commercial plant later. It is hardly necessary to say that for what apparatus may not be available, simple substitutes can usually be found. On the other hand, it is more likely that additional apparatus will be added if any serious work is undertaken, such as an accurate balance, filter pump, viscosimeter, proper temperature control, some means of pH determination, etc. In connection with thermometers, the advice is given to spend liberally on good quality ones that can be easily read. Except with "boiled" emulsions, temperatures above 140° F. (60° C.) are rarely needed, and if a short-scale type be used, the readings will be correspondingly clearer in the darkroom. Eimer and Amend (New York) make a student's type 30 cm long, reading from $+10^{\circ}$ to $+110^{\circ}$ C. and $+20^{\circ}$ to 220° F., marked either on the glass stem or on a paper scale inside the outer glass. Both types can be obtained with a short scale reading from 0° F. to 130° F., which is a great convenience. Note that chemical thermometers scaled for total immersion are not suitable for general work. Thermometers of the clinical type, with a broken thread of mercury so that a temperature taken will remain recorded until the mercury is shaken down, are very useful. These can be obtained with any temperature range if specially ordered through a maker or scien-

tific apparatus dealer. It is often recommended that the bulb should be protected by a perforated gauze of some non-reacting metal, but probably the best way to safeguard thermometers in emulsion work is not to use them as stirring rods!

Emulsions are ordinarily made in stoneware or earthenware crocks, and these are not easy to obtain in small sizes except from scientific apparatus makers and some of the larger department stores. Glazed stoneware jars, sometimes used as "waste jars" in laboratories, can be obtained from Eimer and Amend in sizes from 1 gallon capacity upwards, this size being $7\frac{1}{2}$ inches high and $7\frac{3}{4}$ inches outside diameter, and costing, with loose stoneware cover, just over a dollar. The experimenter will, however, require smaller sizes, and such crocks, with covers, of one pint, one quart, and half-gallon capacity should be obtained. For very small mixings there is nothing so convenient as a small well-glazed earthenware casserole pot of the tall, not squat, type. These can be had on searching diligently enough at some of the hardware and department stores. At least one large stoneware jar with hole or "tubulure" at bottom must be available for washing emulsions (see p. 70). A one-gallon jar will suffice for washing any negative emulsion that is to finish up not more than one liter (35 oz.); a two-gallon jar will suffice for lots of two to three liters. Rubber corks should be used for the bungs, but they should be washed with hot soda water before use.

Glass stirring rods should be twelve inches long and at least one-half inch in diameter. A stout stirrer that can be gripped firmly so that good wrist action can be applied, which is stout enough to beat up the emulsion thoroughly, is quite an important item. Stirring rods with rubber guards should *not* be used.

Scales and weights must be reasonably accurate, as such small quantities as fractions of a gram have frequently to be weighed. Some sixteen-ounce and thirty-two-ounce bottles are

useful for stock solutions. Graduates ranging from ten cc to 500 cc should be available, and some Pyrex or glass beakers of 100 and 250 cc capacity. Pyrex beakers, student's pattern, graduated in clear figures, can now be obtained which are almost unbreakable, cheap, and approximately accurate for general work. One or two plain filters, thirteen to fifteen cm outside diameter (250 to 500 ml capacity) will be needed, and a couple of separatory funnels if mixed jet emulsions (p. 100) are to be made.

As most solutions are used hot, it is important to have sufficient heating facilities for getting the various items ready for emulsification. Depending on the size of the operation, anything from a large aluminum saucepan to a steam-heated rectangular wooden or stainless steel tub with heavy service immersion heater can be used. A metal heating pan about sixteen by twenty inches and about eight inches deep is a very convenient size for experimental work, with either an immersion heater or a small gas ring underneath. Either can be easily thermostatically controlled. For small single lots of emulsion, an aluminum saucepan standing on an ordinary domestic type of electric heater will answer quite well. In many laboratories, existing equipment will meet the case, provided it can be kept sufficiently free from contaminating influences.

A good laboratory stop-watch is invaluable if any serious work is intended. As important as the watch is a really good darkroom clock, which can be depended on to ring the alarm bell when a pre-set time has expired. A little extra money allocated to the clock will be found a good investment. In preference to the use of luminous hands and dials, it is recommended to place the clock on a small box fitted to the wall, a strip of dark green safelight being inserted in the top (Fig. 10) through which light from a ten-watt lamp at the bottom of the box passes upwards on to the dial and makes it just sufficiently visible. A

small projecting piece, *P*, will prevent any light spreading to the room. A metronome is exceedingly useful for counting seconds when working in complete darkness or very feeble panchromatic light.

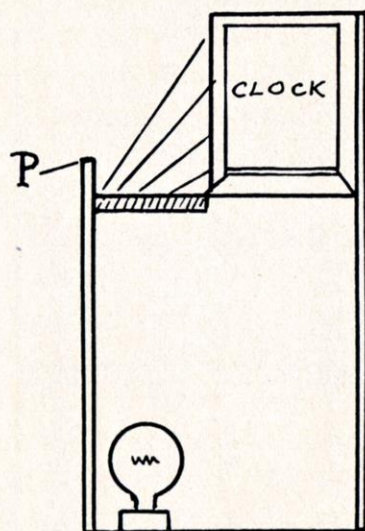


FIG. 10

If the student of emulsion technique wishes to study grain growth and morphology, a first-class microscope outfit will be required. A low power is useful for studying mechanical defects and large developed grains and grain aggregates, but for any examination of silver halide crystals a $\frac{1}{2}$ -inch oil immersion objective is needed. Photomicrography of silver bromide crystals can be done with surprising success without the use of any photomicrographic apparatus except a ninety-degree prism on the eyepiece. This simple technique has many advantages over elaborate equipment. The microscope, with its mirror removed, is placed on top of a light-tight box, with an aperture about an inch and a half in diameter, *H*, (Fig. 11) cut out in the top. A lamp *L* (Pointolite or concentrated filament

type) is placed underneath, in the box. The rays thus pass directly upwards to the Abbe condenser. The small eyepiece prism, *P*, deflects the rays at right angles on to the wall, where a plate, *AB*, is stood on a suitable ledge or support, and receives the image. Final focusing of the crystals is thus done actually

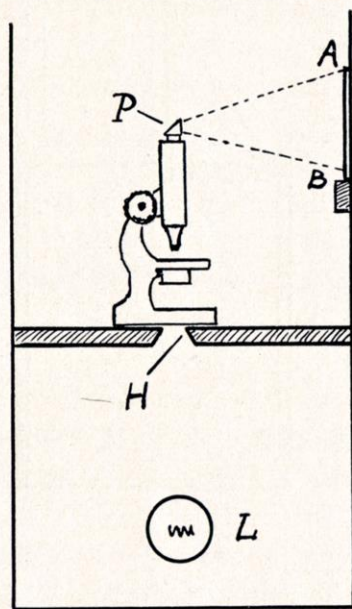


FIG. 11

on the plate, and all that has then to be done is to switch off the lamp (or insert a filter in the light path), replace the plate *AB* by an unexposed one, and make the exposure. When the eyes get accustomed to the complete darkness in which this work must be carried out, exact focusing can be done quite easily. A bit of dead-blackened brass or a cardboard tube between the aperture in the top of the box and the Abbe condenser will prevent any extraneous light from fogging the plates. As with high power an image of the light source should cover the whole field, a good alternative to the Pointolite is one of the flat strip in-

candescent lamps used in sound recording, which runs from a six-volt storage battery taking about thirty amperes. These lamps are obtainable from the General Electric Company.

While, for cooking or digesting purposes, Thermos or Dewar flasks are most convenient for small lots of emulsion, a thermostatically controlled pan is more or less a necessity if work on any serious scale is to be undertaken. A metal pan similar to that already described for heating solutions will be convenient, but as it will be required at a lower temperature it should be a separate piece of apparatus. A deepish pan sixteen by twenty inches and twelve inches high is a convenient size. This can be kept filled with water to a height of five or six inches, or within an inch and a half or two inches of the top of the smallest crock used. For uniformity of work, standard-sized lots of emulsion should be made as far as is possible, so that the water level in its relation to the amount of emulsion is kept fairly constant. In other words it would be bad practice to have a half-gallon crock eight inches high standing in only three inches of water, even if the contents were kept well stirred.

Such a metal pan can be fitted with a hinged lid unless the emulsions are to be stirred during digestion. In some commercial plants, where very long digestions are given at a low temperature, it has been found best to digest or finish without stirring, the whole of the bulk gelatin having been added and dissolved beforehand so that sedimentation is reduced to a minimum. Any coarse grains which do settle can be largely eliminated by careful decantation or suitable filtering. On the other hand, Carroll and Hubbard state ¹ that in their experiments all emulsions were stirred continuously during digestion to prevent sedimentation. Similarly Trivelli and Sheppard state ² that "the object being to obtain a uniform, relatively fine-grained material, silver halide emulsions are continuously and thoroughly stirred." With short-timed finishing of very high-speed

emulsions having a long scale of gradation, it is the author's experience that the crock should be left unstirred in the digesting pan, but every formula has its own particular optimum conditions and no fixed rule can be even suggested.

The apparatus needed for washing small lots of emulsion will depend entirely on the bulk that is to be handled. In a number of the formulas given in this book, a small unit of about one liter is set out, which can be multiplied as required for commercial bulks. The bulks used in manufacture, as elsewhere stated, may run up to fifty or sixty gallons in the case of paper emulsions, while fast emulsions are generally made in smaller units which are blended for better uniformity. It may be pertinent to refer here to what appears to be a very indiscriminate mixture of grams and ounces, liters and gallons, centimeters and inches, Fahrenheit and Centigrade. The metric and avoirdupois systems have become inextricably mixed in the industry, and any reference to photographic literature indicates that the two systems are so much in use that alternative figures have to be given. The gelatin manufacturer sells his gelatin by the pound, rarely by the kilo, even in Europe; dyes are sold by the pound and in ten-gram or one-hundred-gram lots; silver nitrate is bought largely in 1000-ounce parcels in England, but is meticulously dissolved up in the factory in the form of bi-normal or tri-normal solutions which are measured by metric system for use. And so it goes on. In most cases temperatures have been given in this book in both Centigrade and Fahrenheit figures.

To return to the washing apparatus. The stoneware jars referred to on page 43 will be found ideal for washing small lots, but as explained later tanks are used for commercial batches. As good washing depends on getting the noodles in as intimate contact with the water as possible, their gentle agitation in each change is necessary. The agitation can best be done by gentle stirring with a glass rod or spoon, keeping the shreds well sepa-

rated without breaking them. At the end of each change, the water is run off, provision being made that no shreds escape through the outlet. A false bottom of suitable textile material may be used, so that when the wash water is run off the noodles can be thoroughly drained. When washing is complete, draining should be made as complete as possible. It sometimes happens in washing that the gelatin takes up so much water that on remelting the volume is greater than the desired amount. This will lead to thinness of image and frequently to fog. The remedy is to use colder washing water, to use a less absorbent gelatin, or to decrease slightly the bulk of the reacting solutions in mixing. It is good practice in the laboratory in hot weather to throw in a few ice cubes with each change of water if the temperature of the darkroom cannot be controlled.

It will be noted in the formulas which follow that about five per cent of alcohol is included in the "finals." It will be found good practice to pour this alcohol on the washed noodles after they have been transferred to the crock, and before starting to melt up. This accelerates melting, which is good practice, as it confines the final digestion or finishing within stricter control. The crock should therefore be stood in really hot water, 160° or 180° F. and the emulsion kept well stirred, so that the shreds nearest the outside of the jar do not get raised to a higher temperature than those in the middle. When the emulsion temperature has reached 105° F. (40° C.), it should be removed from the water, because the jar itself will be hotter, and a further rise in temperature of the contents will take place. Great care must be taken, in fact, that the temperature of the emulsion is not allowed to exceed that of the final digestion temperature, and that as soon as this has been reached, the crock is transferred immediately to the digesting pan. When the digestion is finished, the emulsion should be poured into a cold crock and the finals added. These are usually chrome alum solution to

harden the film, free ammonium or potassium bromide to prevent edge-fog in plates and fog on keeping (in the case of films and papers), a preservative such as carbolic acid, thymol, sodium salicylate, etc., and any such gelatin-plasticizer as glycerin.

The made-up emulsion is now filtered, and for laboratory scale operations nothing better can be recommended than two to four thicknesses of good quality cambric or linen which has been boiled in order to remove any sizing. A fine quality men's handkerchief is excellent for the purpose. Filter paper is useless; chamois leather is not advisable, as it is usually uneven in thickness and the emulsion merely runs through the thinnest part. If suction is available, such as that from a good filter pump attached to a faucet having a good head of water, a Buchner funnel will be found very useful. It may be questioned why, when chemicals of the highest purity are employed, any filtration should be needed. Leaf gelatin contains a good deal of string fiber, unless dried on wire nets; if ground, it will contain a surprising amount of dust and dirt. Even re-crystallized chemicals contain some dirt, and an examination of the filter cloth, after the emulsion has run through it, will reveal the need for filtration. In addition to mechanical dirt, filtration goes a long way towards breaking up *clumps* or aggregates of silver halide grains, which are always formed to a more or less extent in the process of making.

If the cambric or linen is laid over the top of a clean crock, it should be attached by a piece of twine or tape tied tightly around the top edge. The linen is gently pressed downwards to form a bag, and the emulsion is poured into the bag, and filtering helped with a glass stirring rod. If the emulsion is obdurate, a vacuum can be created in the crock by pulling the linen tight with the hands; this has the effect of drawing the emulsion through. It is the usual practice to coat a test plate

at this stage, and then to set the emulsion off in ice water, remelting it again a day or so later when required for coating. Emulsions will usually keep for several days, or even weeks, if stored in a room kept below 45° F.

We can now give some attention to work on a larger scale, where somewhat different handling of the emulsion will be required. While the "unit" lots described in subsequent chapters may be increased by simple multiplication, as the bulk grows larger various modifications must be made in order to prevent overheating. One of the most successful pioneer dry-plate manufacturers always claimed that it is possible to produce in one liter (35 oz.) all the qualities and speed of a works-size batch of emulsion, and this is correct provided that works batches are made in moderate units, such as two to three gallons and not in bulks of fifty to a hundred gallons. When planning works-scale operations, it is advisable to decide on the policy to be adopted; that is, whether to make in comparatively small lots of two or three gallons and mix these at a later stage for coating, or to manufacture in bulks of five or ten times this size. The difference in sheer mechanical handling that is involved must be obvious. Convenience in handling is much greater if moderate quantities are made at the time of emulsification, and blended after washing. The shreds can be mixed after washing, and remelted as a blend, or each small unit can be carried through to the end and tested *before* blending, which is a surer way of obtaining perfect uniformity of product.

In the commercial manufacture of films, plates, and papers, two things of first importance stand out — freedom from dust, already discussed, and adequate control of humidity and temperature. It unfortunately happens in many cases that a building designed for some other purpose is adapted for the making of sensitized products. Such a building is rarely as efficient or satisfactory as one which has been specially designed. On the

other hand, many factories which the author has visited in Europe show signs of continual additions due to trade expansion, where compromises have clearly had to be made. One noteworthy difference between a plate factory and one for film or paper coating, is in the length of building required. While plates will set in half a minute on a thirty-foot machine, and can be lifted off and stacked in cupboards to dry, both film and paper have ordinarily to be run from the coating head to a drying tunnel where the material hangs in loops or festoons and travels slowly along the track for anything from three hundred to six hundred feet. Being dry by the time it reaches the far end, it can be immediately re-reeled, thus making the process a continuous one, which is frequently carried on three eight-hour shifts a day for days at a time. Koebig's catalogue³ gives particulars of a film coating machine which winds the coated stock in the manner of a spiral, thus greatly conserving space.

Whatever the product may be, we are concerned in this chapter more especially with the emulsion-making department. Here the importance of cleanliness must be again emphasized. Ample space is most desirable. Temperature control is indispensable. The layout already discussed for small-scale operations needs merely to be amplified and elaborated. In many factories, the work is distributed among several buildings, each complete in itself. Each one has then its own emulsion-making laboratory to feed the particular coating room. This system, by the way, has the great advantage that if, as occasionally happens, some chemical or other trouble arises, it hampers work in only one section of the factory.

If the whole laboratory layout can be on one floor, so much the better, as then the various rooms can be arranged in definite sequence, so that stores and weighing rooms are the commencement, and the finished emulsion comes out at the end. The store for chemicals and gelatin should be arranged so as to be conven-

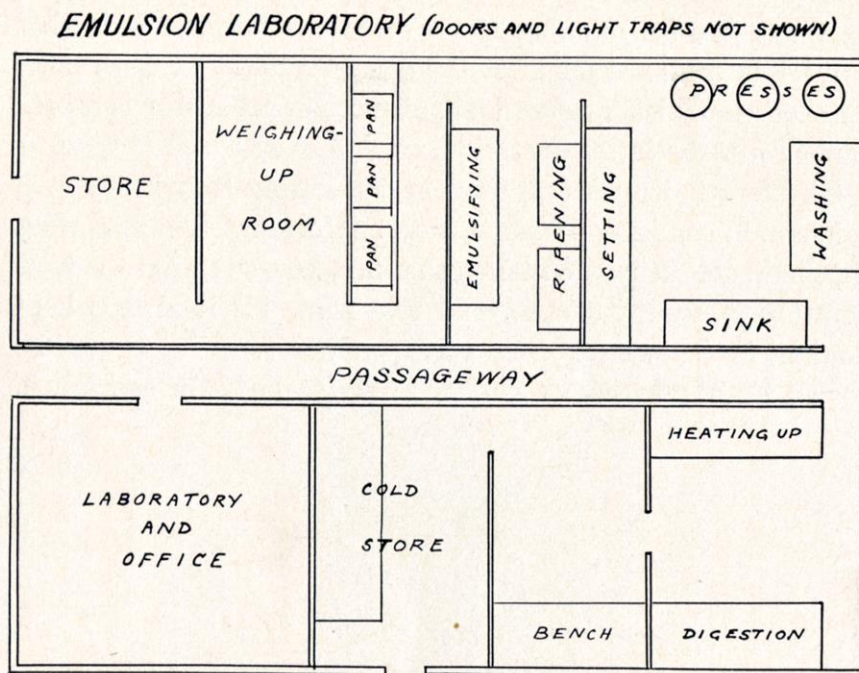


FIG. 12

iently situated for unloading goods. The finished emulsion can be wheeled in small light-tight trucks from the making-up room to the building where the coating is done. A suggested plan is seen in Fig. 12, where the store leads into the weighing room, and the crocks and silvers are heated for mixing in a small compartment next to it. The emulsification is then carried out on the bench in the next compartment, the emulsion placed in the warm water pans to ripen, and then set in the cold tanks in the end room. It will be noticed that in the emulsifying room two ripening pans are shown. In many emulsions of the "all-ammonia" type, emulsification is carried out at a low temperature and when the bulk gelatin is added, the emulsion must be raised to about 105° F. as quickly as possible, in order that it may be properly dissolved. It is often necessary, therefore, to

have one pan for ripening at the lower temperature and a hot pan for heating the jar after the gelatin addition. With large batches of emulsion, some form of mechanical stirrer is a convenience in the latter operation.

The term "ice water," used in the setting troughs, is very common in emulsion parlance, but is unfortunately a somewhat slipshod one. It may be taken to mean, however, that the temperature is around 36° F., and that some ice is always kept floating in the water. The cold pan water can of course be cooled by a refrigerator coil and thermostatically controlled.

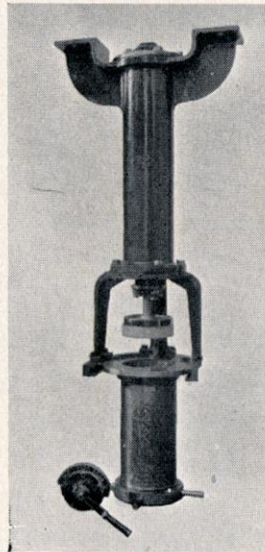


FIG. 13

The set emulsion, which may in some cases be washed in from three to five hours, though more generally the next day, is pressed into noodles or shreds in the setting-off room by the presses indicated. The noodles are most conveniently washed in the same department. As considerable quantities of water must be handled in the washing process, a cement or composition

floor and walls which can be hosed down, with good gutters running to an ample waste, should be provided. Large faucets are needed to expedite the refilling of the washing troughs, and a suitable water main with ample pressure will be needed to insure the necessary hydraulic pressure for the shredding machines.

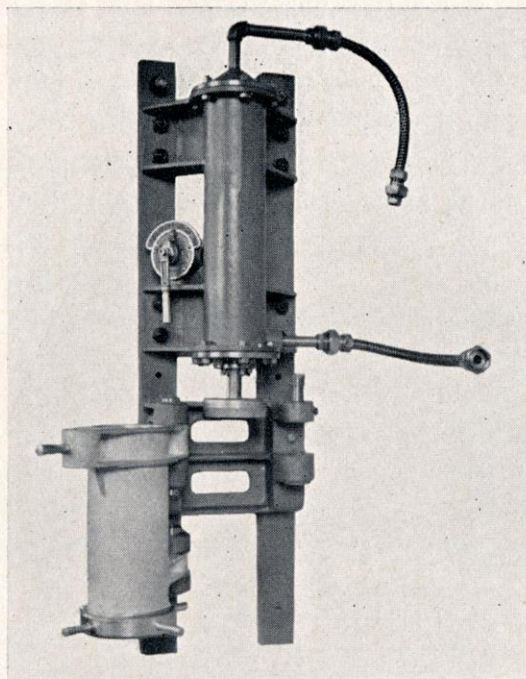


FIG. 14. FLOOR PRESS SHOWING EMULSION CONTAINER SWUNG OUT FOR LOADING WITH JELLY

These presses may be attached to a wall fitted in a strong steel frame for suspension from the roof (Fig. 13) or can be fixed in wooden frames on the floor. The emulsion container is usually made so that it can be swung clear of the pressure cylinder for charging, as shown in Fig. 14. This represents a

Dixon⁴ press, which is constructed of gun metal, with a piston rod of stainless steel, and a plunger cap of nickel fitted with a wooden face. The emulsion container (seen swung out for charging in the figure), is lined with pure nickel, and the perforated shredder plate, which drops into the bottom of the container, may be made of pure nickel also. This plate, having perforations three-sixteenths or one-fourth inch in diameter, must be very stout so as to stand up to the force of the cold jelly when squeezed through it. A sterling silver shredder plate is strongly recommended by the author.

The washing tubs, which receive the noodles as they fall from the press, may be of wood or stoneware. If the latter, they

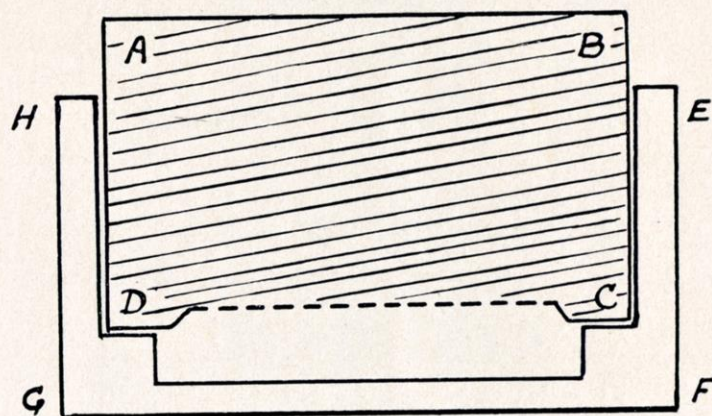


FIG. 15

should be provided with wooden trestles which can be wheeled easily to the part of the room where washing takes place. Considerable divergence of opinion exists as to the best method of washing. If four volumes of water are allowed for each volume of emulsion (before shredding) and the noodles are kept sufficiently separated by wooden paddles or some simple and gentle agitating device, and the wash water is thoroughly drained off after each change, it will be found that twelve changes of five

minutes each, with three minutes draining, will adequately wash practically any type of emulsion. Three or four hours are recommended by some writers, but this tends to over-swell the emulsion and affect its character.

One form of washing trough is shown diagrammatically in Fig. 15. Here an inner wooden tub, *ABCD*, with gauze or canvas bottom drops into an outer trough, *EFGH*. The inner vessel is about one-third filled with noodles, and water is fed into it until it well covers them. In draining, a small loss of emulsion is inevitable, as, in mechanically keeping the shreds separated, small bits are bound to be broken off and pass through the screen at the bottom of the tub. The loss in washing should not exceed one to one and one-half per cent. Cold water, never above 55° F., should be used.

The washed shreds, as explained later, are remelted and subjected to a process of digestion during which the speed increases very greatly, and while in most cases the temperature used lies between 120° and 125° F. (about 49° to 52° C.), it may be considerably more in the case of slow emulsions, or of course of "boiled" emulsions (p. 6). A type of digesting pan which can be made on a small laboratory scale or on a works scale is seen in Fig. 16. The emulsions crocks stand in an inner rectangular pan of metal which in turn stands in an outer one. Both contain water. A thermostat shown in the inner pan controls a fairly heavy heating element, via a suitable relay, which is fixed at the bottom or at one side of the outer pan. If no stirring is to be given, the crocks may be covered with loose lids, but in many cases vertical stirrers are fitted to a loose cover on top of the pan, as shown in the diagram. These are motor driven, and turn only fast enough to prevent sedimentation.

Some ingenuity must be used to take care of condensation water dropping from the bearings of the stirrers or elsewhere into the crocks, which could easily fog the emulsion by chemical

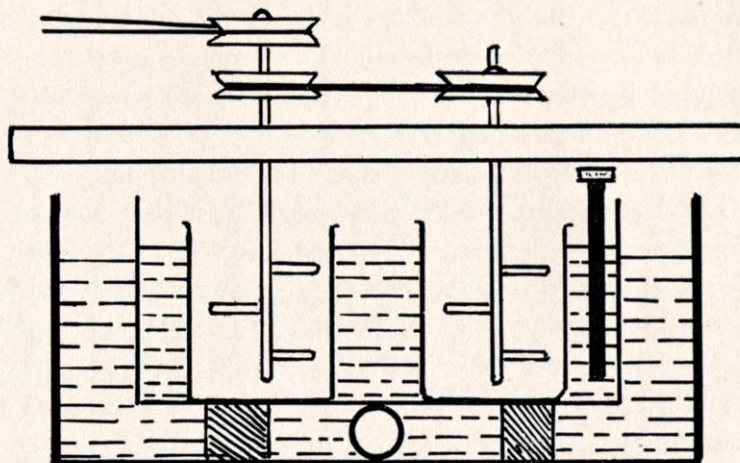


FIG. 16

contamination. Some form of loose cover for the crocks themselves as well as an overhead guard will combine to give the necessary protection. Needless to say, the apparatus can be simplified by having one pan only of water, the thermostat and heating element being contained in it along with the emulsion. It is then an advantage to have the outer water itself stirred to insure an even temperature.

The thermo-regulator should be capable of a range of control of between 110° and 140° F. (45° and 60° C.). An immersion electric thermostat consists usually of a thin metal tube hermetically sealed at the bottom, which contains a sensitive bimetallic bar that extends from the bottom about half-way up the tube. The contact points are protected by a condenser to prevent sparking. The control temperature is often regulated by a removable key so that, once set, it cannot be tampered with or altered accidentally. Care must be taken that the thermostat is capable of handling the load required, which will of course depend on the bulk of water involved.

Reference has been made in an earlier part of this chapter to Thermos flasks. For test lots of emulsion in the factory,

these are very handy and deserve some further notice. The flask should be filled with hot water several minutes before it is needed, at a temperature two or three degrees higher than the digestion temperature. If the emulsion when put into the flask is also a couple of degrees higher in temperature (Fahrenheit), it will probably drop to the desired point or a trifle below during digestion, the figure over the total time averaging out very nicely. A practical point that should be emphasized is that thermostatically controlled apparatus will operate most satisfactorily in a room where the temperature does not undergo drastic variations. Where the laboratory is maintained throughout the year at about 70° F., very little difficulty will be found in controlling water baths and pans.



FIG. 17

60 PHOTOGRAPHIC EMULSION TECHNIQUE

The digested emulsion must be made up as quickly as possible, and this is done by (a) lowering the temperature to 105° F. or below, and (b) adding such final additions as chrome



FIG. 18

alum, alcohol (if this has not been already added), potassium or ammonium bromide, and any other chemicals. The speed then stays put more or less, and the emulsion can be filtered and sent to the coating room or reset and put into cold storage until required.

Filtering can be done by gravity, or with the help of either pressure or suction. A typical example of a pressure filter is the Dixon model,⁴ which is an enclosed cylindrical vessel of 960 ounces capacity, fitted with a perforated metal plate for

the support of the filtering medium, and an air valve for connection to a pressure pump. It is designed for use upon a metal or wooden table support, under which the emulsion jar or receiver can be placed. It is seen opened out in Fig. 17 and closed for use in Fig. 18. Two forms of suction filtering plant are seen in Fig. 19 and Fig. 20. In the first of these an inverted funnel, over the top of which is tied the filter material, is placed near the bottom of the receiving jar. The tube of the funnel, and a bent glass tube leading to a suction pump, fit tightly into a rubber cork in the neck of the receiver. Moderate suction is applied to the bent tube. The other type is made by a well-known firm of earthenware manufacturers.⁵ This is a jar with outlet pipe for suction apparatus to be connected; a heavy perforated stoneware disc sits on top of the flange of the jar, and above this is a stoneware top. The filtering medium is placed between the disc and the top, and suction provides the seal. Another type of suction filter, made by Koebig,³ is seen in Fig. 21.

When filtering by gravity only, a larger apparatus of the type described on p. 50 is used. The chief difficulty in all filtering of emulsions is the choice of material. Filter-cloth makers

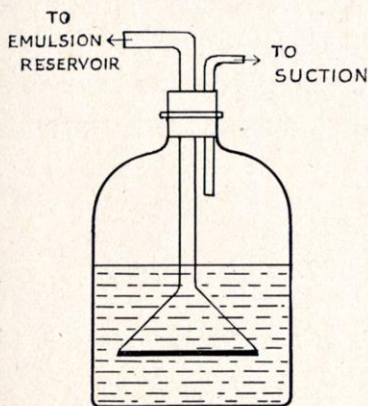


FIG. 19

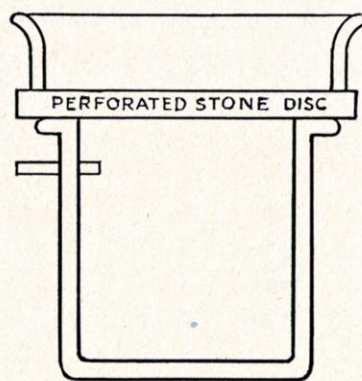


FIG. 20

have a wide variety to choose from, but it will be difficult to improve on the four thicknesses of fine linen or cambric already suggested.

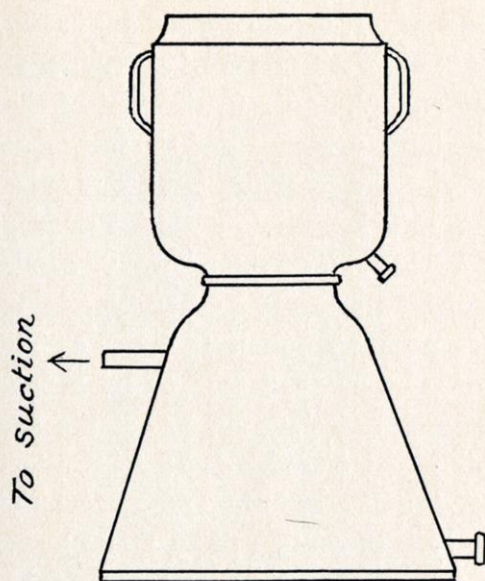


FIG. 21

The filtered emulsion is quickly set, and for this purpose it can be returned to the setting tanks in the washing room, or preferably to a separate cold room, where the temperature can be automatically maintained at somewhere below 45° F., or the jars can be stored in ice water or cool cupboards. The time that made-up emulsion can be safely stored, depends entirely upon its previous history.

Chapter References

1. Carroll and Hubbard, *Bureau of Stands. Journ. of Research*, 7, 226, 1931.
2. Trivelli and Sheppard, *The Silver Grain of Bromide Emulsions*, p. 32.
3. August Koebig, Radebeul, Germany.
4. Thomas Dixon and Sons, Ltd., Letchworth, England.
5. Doulton and Co., Ltd., Lambeth, London, Eng.

CHAPTER IV

NEGATIVE EMULSIONS

Their Structure and Composition — Types of Formula — Preparation of the Reacting Solutions — Emulsification — Ripening — Setting — Washing — Final Digestion or Finishing — Making up — Anti-halation Methods — Reversal Emulsions

A NEGATIVE type of emulsion of moderate speed is probably the most suitable to select for a first consideration of emulsion making. The speed and average grain size and some other properties of the slower types of emulsion are as follows:

<i>Type</i>	<i>Relative Contrast</i> γ	<i>Resolving Power</i>	<i>Latitude</i> *	<i>Speed H & D</i>	<i>Average Grain Size</i> microns
Transparency					
or lantern	3.2	100	25	5	1
Process	3.0	90	25	20	1.5
Photogravure	2.8	80	40	40	1.0-2
Commercial	2.2	65	75	90	1.5-2
Motion picture					
positive	2.7	80	50	150	1-2

* Ratio of exposure at limits of the straight line portion of the characteristic curve for development to gamma infinity. In many cases this portion is measured between the points where gamma is 0.5 at the toe and shoulder.

In so-called grainless emulsions of the type described on page 136, the mean diameter of the grains (AgBr crystals) is of the order of 0.0002 mm, or 0.2 μ . While speed and grain size do not necessarily increase side by side, the grains of fast emulsions are generally larger than those of slower ones, reaching 3 to 4 μ , although the diameters are invariably mixed. Thus

64 PHOTOGRAPHIC EMULSION TECHNIQUE

Clerc¹ states that in a particular emulsion the distribution between the different sizes has been found to be as follows:

Less than 1 μ	61 per cent
From 1 μ to 2 μ	32 per cent
From 2 μ to 3 μ	6 per cent
Above 3 μ	1 per cent

In a slow emulsion for reproduction purposes the extreme ratio of diameters was found to be not more than one to five.

A number of rapid emulsions dried in air (containing an equilibrium amount of moisture of not more than 15 per cent) showed on analysis to average:

Water	10 parts by weight
Gelatin	55 parts by weight
Silver bromide	32.5 parts by weight
Silver iodide	2.5 parts by weight
	100 parts

Traces of silver chloride were found. Weigert and Luhr state that they found as much as 2 mg per square meter of free silver metal. Silver chloride is almost impossible to exclude, as samples of ammonium bromide may contain as much as two per cent of chloride. A good sample of NH_4Br for negative emulsions should not contain more than 0.2 per cent. The slower types of emulsion being considered in this chapter would ordinarily contain about half the above proportion of silver iodide, or less. As chemical analysis (p. 231) of a slow film indicates a coating weight of some 60 to 90 mg of silver halide per square decimeter, the skeleton of the emulsion may be built up somewhat as follows, it being assumed that a liter of emulsion would be distributed over, say, 150 plates of 5 by 7 inches size, or a twenty-foot run of film base forty-two inches wide. For convenience, the amounts of alkaline halides required to convert one gram or part of silver nitrate are given in the table which follows on the next page.

*Reacting proportions of halides to combine with one part of silver nitrate,
AgNO₃ (molecular weight 170)*

Ammonium bromide, NH ₄ Br mol. wt. 98	reacting amt. 0.576
Potassium bromide, KBr mol. wt. 119	reacting amt. 0.700
Ammonium chloride, NH ₄ Cl mol. wt. 53.5	reacting amt. 0.373
Potassium chloride, KCl mol. wt. 74.5	reacting amt. 0.431
Sodium chloride, NaCl mol. wt. 58.5	reacting amt. 0.408
Ammonium iodide, NH ₄ I mol. wt. 143	reacting amt. 0.617
Potassium iodide, KI mol. wt. 166	reacting amt. 0.638

Bearing in mind that the emulsion must be washed, during which process the jelly takes up almost its own bulk of water, the final volume of emulsion desired must be about halved in the making.

Formula for 1 liter of emulsion (1000 cc)

A. Water	350	cc
Ammonium bromide	32.5	g
Potassium iodide	0.5	g
Gelatin	10.5	g
B. Silver nitrate	25	g
Distilled water	5	cc
Ammonia (conc.)	a sufficient quantity to redissolve the precipitate of silver hydroxide first formed (this will require about 25 cc of ammonia of 0.920 s.g.)		
C. Silver nitrate	25	g
Distilled water	110	cc

Here we see that about 500 cc of water is divided between the salts and silvers in the rough proportion of 35 to 15. The bromide is used in about 8.5 per cent excess of the combining quantity. The iodide is present in the proportion of one per cent of the weight of silver nitrate. The gelatin in this case is three per cent of the water in which the salts are dissolved. The silver nitrate is divided into two equal parts, one of which is highly concentrated and redissolved with ammonia; the second half is

used plain, and is dissolved in just over four times its weight of water. Plain silvers should not as a general rule be used in a higher concentration than one to four of water.

The excess of bromide used over the weight needed to combine with a given quantity of silver nitrate varies over wide limits. Wall² quotes cases where the excess varies from 1.9 parts per 100 of silver nitrate (Burton) to 92.4 parts per 100 (Eder). Eder is also quoted as using in different emulsions 8.4, 67.4, and 75.4 parts respectively per 100 above the combining quantities of AgNO_3 , indicating at least that there is a very great tolerance. He states that the explanation usually accepted for the favorable action of the excess bromide is that the finer particles of silver halide are dissolved by the excess and in the course of ripening are deposited on the larger grains (*cf.* Ostwald ripening), thus giving increasing sensitivity. It will be found, however, on studying the earlier literature that a larger excess of bromide was used in cases where all or a large proportion of silver nitrate was redissolved, and this indeed appears to be necessary in order to prevent fog. Only a very small excess is actually needed where the silver nitrate is divided into three or even four parts and added to the salts piecemeal, with very little ammonia, allowing fairly long intervals between additions; or where the iodide is added separately after the first emulsification with silver and bromide only, with or without ammonia, when it appears to act as a peptizer.

The three solutions in the above formula are heated, *A* and *C* to 110°F. (43°C.), and *B* to 70°F. (21°C.). *B* is poured in a steady stream into the crock containing the salts *A*, stirring fairly briskly, the precipitation taking about five seconds. *C* is then at once poured in, this time through a funnel with a three or four millimeter outlet, stirring briskly. After ripening for fifteen minutes, without stirring, or at least giving only an occasional gentle stir, the bulk gelatin is added, *dry*, about 70 g

being used, which will bring the concentration up to approximately eight per cent of the final bulk of 1000 cc. A little gelatin, together with a small amount of the silver halides, is inevitably lost in washing. Fifteen minutes should be allowed for the gelatin to dissolve completely, even if powder be used, the crock being gently stirred the whole time. The temperature must not be allowed to rise above 105° F. (40.5° C.) during this operation, but if the same emulsion be made on several occasions, the same temperature conditions should be repeated as far as is possible. When the gelatin is dissolved, the emulsion is set off by placing the crock in ice water, and giving the contents an occasional stir until gelling takes place.

The above way is a convenient one for expressing the formula, but only one of many. Another, frequently met with in European literature, would be as follows:

- (a) 180 cc gelatin solution 5%
- (b) 162.5 cc ammonium bromide solution 20%
- (c) 5 cc potassium iodide solution 10%
- (d) 25 cc silver nitrate solution 1:1
- (e) 100 cc silver nitrate solution 25%
- (f) 70 g gelatin, dry

This is very approximately the formula already given. It is of course a great convenience to use reacting substances in the form of solutions, especially silver nitrate. In some factories these are made up in the form of multi-normal solutions of which equal volumes are equivalents. In several of the formulas given in this book, where highly concentrated silvers are employed, it will be found more practical to weigh the silver nitrate out.

A further method of setting out a formula is used by Carroll and Hubbard³ in the case of an "all-ammonia" emulsion, and we find that they have expressed it in more academic fashion as follows:

68 PHOTOGRAPHIC EMULSION TECHNIQUE

Water	ml 250	Water	ml 500
AgNO ₃ (0.353 mol) ...	g 60	NH ₄ Br (0.409 mol) ...	g 40
NH ₄ OH conc. (0.71 mol)		KI (0.0035 mol)	g 0.58
	to redissolve	Gelatin	g 30

Excess bromide is seventeen per cent. The halide-gelatin solution was kept at 45° C. ± 0.5° during mixing, which took four and one-half minutes, and during ripening. After ripening for twenty-five minutes, 70 g of gelatin previously swelled in cold water was added, taking seven to ten minutes, and the emulsion was chilled. (The *mol* figures given are obtained by dividing the molecular weight of the substance into the weight used.)

Another distinctive type of emulsion is that recommended by Heyne⁴ for negative motion-picture film. Three solutions are prepared as follows:

A. Gelatin	250 g
Water	3500 cc
Potassium bromide	400 g
Potassium iodide	10 g
B. Silver nitrate	500 g
Distilled water	1500 cc
Ammonia (s.g. 0.910)	about 475 cc
C. Gelatin	500 g
Distilled water	2500 cc

The gelatins in solution *A* and *C* are allowed to swell in the water. The salts are then added to *A* and both solutions are raised to 122° F. (50° C.). The silver nitrate is dissolved in water, and ammonia added as usual, sufficient to redissolve the silver hydroxide. This is used at room temperature and is added slowly to the crock with good stirring.

The emulsion is maintained at 112° — 122° F. (45° — 50° C.) for thirty minutes, when the gelatin solution *C* is added to it at the same temperature. The emulsion is then digested

for a further fifteen minutes, and is set off in ice water. It is stated to attain its highest sensitivity during the digestion after washing or finishing. A temperature of 112° — 132° F. (45° — 55° C.) is recommended for the finishing. In this process a small trace of ammonia may be added. (This addition is *not* recommended by the author unless a second washing be given, when the bulks will require modification throughout, or the pH be lowered to just above normal by suitable treatment with the finals.) During the final digestion, small hand-tests are made at short intervals, and when the maximum useful speed and gamma have been obtained, the usual additions of chrome alum, bromide, spirit, etc., are made. In the case of film coating, one to one and one-half per cent of glycerin may be needed.

Let us assume that the emulsion has been given its correct ripening time, and that the bulk gelatin has been added. It is important that this be very thoroughly dissolved. Powdered gelatin should be "poured" slowly into the emulsion with good stirring; this will avoid its annoying tendency to form into gluey lumps which are troublesome to dissolve. In making small lots of emulsion it will be found a convenience to cut up *sheet* gelatin beforehand into small pieces with a clean pair of scissors. The gelatin melted, the crock or jar is stood in ice water and the emulsion allowed to set. It should always be given an occasional stir until it begins to gel, especially in the case of large batches. These, if of any fast variety, are best distributed over a number of small one and one-half or two-gallon cold crocks to expedite setting. In the case of emulsions where the whole of the silver has been treated with ammonia, washing is usually given within from three to five hours, otherwise ripening goes on in the cold, and fog may result. With emulsions where less than fifty per cent of the silver has been converted, it is customary to leave the emulsion in the cold room until next day. In factory practice it is of course important to have some system

by which the time between emulsifying and washing is kept more or less constant for each type of emulsion. Thus if all-ammonia and part-ammonia types are being made, the all-ammonias can be mixed in the morning and washed in the afternoon, while the others are mixed in the afternoon and washed the following morning. It will be found a convenience to take the set emulsion from cold storage and leave it at room temperature for two or three hours before washing, otherwise it may be unmanageably stiff for shredding. This applies more particularly to small lots or types containing a high concentration of gelatin.

Small lots of emulsion can be broken up with the hand, and pieces of the size of an orange wrapped in a piece of coarse netting (about one-eighth-inch mesh) and squeezed through the material. The netting is such as is used for embroidery work, and must be very thoroughly washed before use, as the sizing will otherwise cause trouble in the way of fogging or desensitization. Various devices used in cooking which can be bought at the hardware stores or department stores have been recommended from time to time for breaking up the emulsion, but the danger here is that the zinc from any galvanized parts will fog it, and although a textile material of sufficiently large mesh is more trouble to use, it is definitely recommended. The jelly comes through the netting in the form of broken shreds an inch or two long, and if the emulsion be held under the water while squeezing it through, the bits or noodles will keep nicely separated. They can then be transferred to the washing jar. A piece of muslin or cheesecloth (also previously washed out) is tied over a jar with a bottom outlet as shown in Fig. 22, the shreds put into the bag formed by the material, and the jar filled with water.

At the end of five minutes the plug is removed and the water run out, and three minutes is allowed for the shreds to drain.

The draining may be made more thorough by teasing the shreds with a glass rod or spoon. The washing procedure is then repeated, and after about eight such changes a test of the wash water with Nessler's reagent will usually reveal that the am-

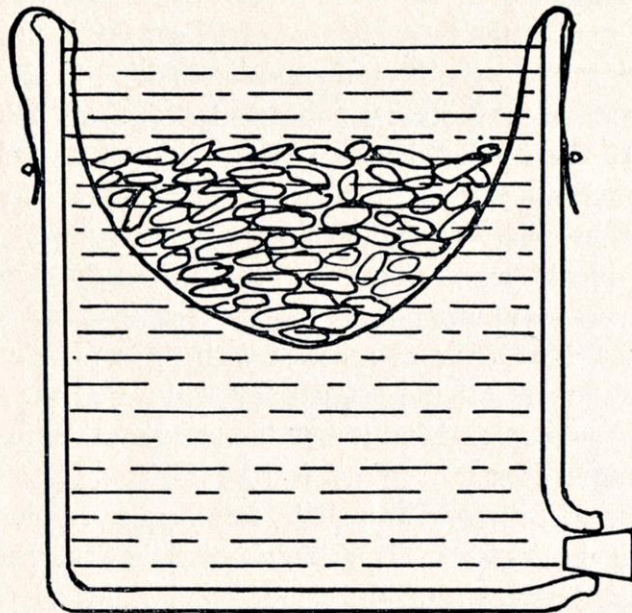


FIG. 22

monia has been eliminated. If not, one or two further changes should be given. The same procedure applies to works-scale washing, but here it is most important to insure that the swelling of the noodles has not been too much, so that on remelting and addition of the finals, the bulk is too large. The best practice is to use tared crocks or nickel or stainless steel pans, and to weigh the emulsions rather than measure them with a stick or any form of graduation.

Considerable difference of opinion exists as to the best length of time for washing. Bogue found⁵ that the swelling and viscosity of a gelatin, which are their minimum at a pH of 4.7, in-

crease regularly with a rise in pH up to about 8.5, but that above that value they decline slightly, due to an increasing solubility. As washing proceeds, and the pH becomes lowered, the swelling is probably reduced, and it is advisable to get rid of the great bulk of ammonia in the first stage of washing by quicker changes, making the later changes of longer duration. It was customary in the early days of emulsion-making to give several hours; more recent literature indicates two and one-half to four hours. If the noodles be kept thoroughly separated during washing, and are carefully drained in the intervals between the water changes, sixty to eighty minutes should suffice, except in cases of highly ammoniacal or of color-sensitive emulsions where any excess of bromide may retard sensitization. The final wash water should give no reaction with silver nitrate as compared with a control; the Nessler test will reveal the presence of residual ammonia. Here it may be stated that distilled water for washing has not proved satisfactory in general practice. In most cases poorer speed and slight fog seem to result from its use. That the character of an emulsion can, however, depend in a remarkable degree upon the characteristics of the local water used for washing is well proven. Wash water has in certain cases been prepared by adding to distilled water the ingredients found by analysis in a natural water which has proven satisfactory. But as a general rule the town supply, or supplies from artesian wells, will be found perfectly good. The presence of mineral salts affects to some extent the swelling of gelatin. Patents have been granted for the buffering of emulsions, maintaining the hydrogen ion concentration within a range of pH 5 to 10 by various additions, as disclosed in recent Kodak patents.⁶ The pH of the washed negative emulsion may vary between 7 and 8.5, though acid emulsions will of course have a lower pH.

A method adopted by Carroll and Hubbard⁷ for shredding

small lots was to set the ripened emulsion by pouring it in a layer of one cm to two cm thickness into a clean enameled tray floated on water at 5° to 8° C., and leaving it overnight. The jelly was then pressed through a sieve built up from sharpened metal strips set on edge, which cut the emulsion into clean shreds five to six mm in cross section. The shreds were placed in silver-plated cans with twenty-per-inch mesh screens of pure nickel at the bottom. The washing was stated to be very thorough, lasting six to eight hours, with frequent hand stirring of the shreds. In the absence of ammonia in the emulsion, the pH after washing was 7 ± 0.5 ; if made with ammoniacal silver oxide the pH might be as high as 8.5.

The emulsion shreds having now been washed so that they consist of merely insoluble silver halides in gelatin, they are remelted in a water bath, and any final additions made. In remelting, a good bulk of really hot water is desirable, so that the noodles melt as quickly as possible. The temperature must nevertheless be kept within a degree or two of that at which the digestion is to be carried out, especially in the case of fast emulsions. The remelting is an essential part of the process of making, and it is highly important in routine work to control the temperature employed, and the overall time taken. As already indicated, an alternative to remelting a number of small batches is to blend the washings from a number of crocks and remelt in bulk.

The final digestion or finishing is carried out in thermostatically controlled water baths such as have been described in the previous chapter. Although there is actually no specific connecting link between final speed and

Time \times Temperature

of cooking, it is certain that above 120° F. (49° C.) some critical stage is reached where sensitivity very rapidly increases.

The temperature of the finishing is another matter on which some divergence of opinion exists, but this is rather because the critical point depends so much on the particular formula. One might hazard the generalization that fast negative emulsions made with ammonia are best digested at a temperature not above 125° F. (52° C.), while slow emulsions, and particularly those prepared with acid, are best treated at 160° F. (71° C.) or somewhat under. The finishing time may be as short as half an hour in the former type, or it may run into three or four hours in the latter. This can only be a very rough comparison, and the extent to which the time may be shortened by raising the temperature is a matter that must be found entirely by experiment for each individual emulsion formula. Probably less sedimentation takes place at the higher temperature and less time, in spite of a lowered viscosity of the gelatin.

An interesting example of the effect of the final digestion upon speed is shown by the curves given in Fig. 23. The fact that washing was in this case done by centrifuge does not interfere. Four lots of one particular emulsion, ripened initially for (*a*) 5 minutes, (*b*) 30 minutes, (*c*) 60 minutes, and (*d*) 120 minutes, were digested after washing for periods up to two hours. It is seen that while in all cases there is a tendency for the speed to rise to a maximum and then to fall off, the highest speed is obtained when the ripening has been longest. With increase in ripening time, however, the regression of the speed after the maximum has been reached is more pronounced.

In discussing the effect of grain size on the finishing of emulsions, Trivelli and Smith⁸ state that before starting the finishing operation, which was done at 60° C. (140° F.), the emulsions, with the addition of gelatin and water, were brought up to a fixed weight and to the same temperature, 40° C. (104° F.). "In this condition," they say, "the emulsion is in its lowest state of sensitivity." They further state that the increase in

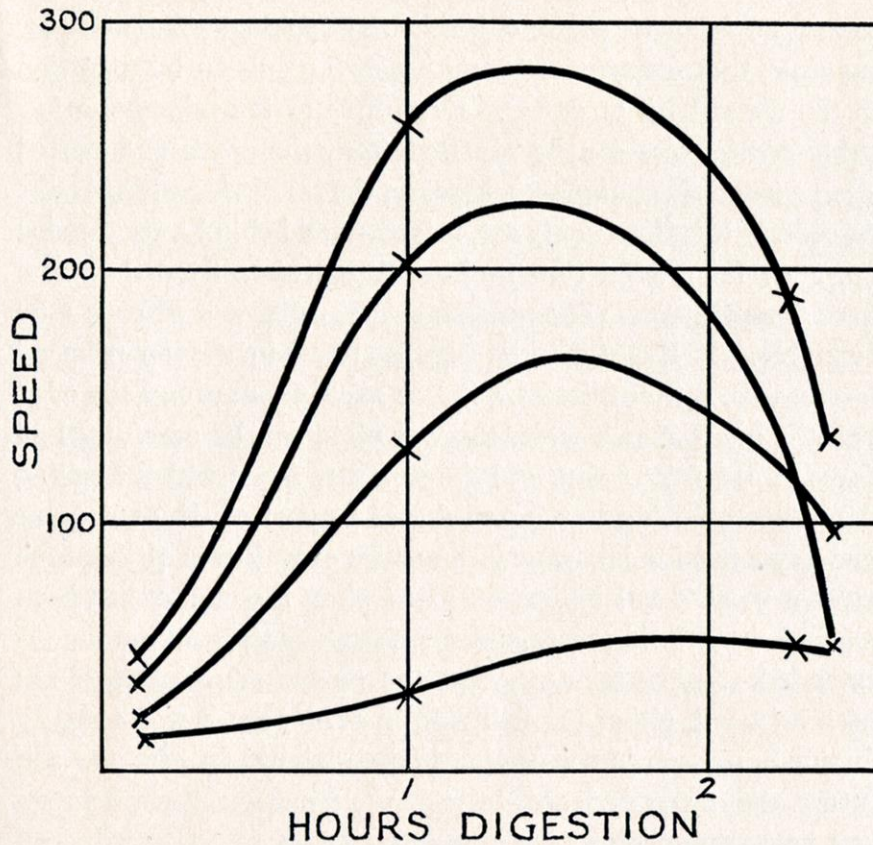


FIG. 23. SPEED OF CENTRIFUGED AMMONIA-PROCESS EMULSIONS AT FOUR TIMES EACH OF RIPENING AND DIGESTION. Ripening time (reading up from bottom) curve (a), approximately 5 minutes; curve (b), 0.5 hour; curve (c), 1 hour; curve (d), 2 hours. (Carroll and Hubbard)

speed can be expressed by the ratio between the H and D speed obtained after digestion at 60°C . and the speed measured at 40°C . Similarly the increase in gamma can be expressed by the ratio between the gamma obtained after digestion and the gamma measured at 40°C . *before* digestion.

It may be said, by and large, that the time required for finishing or final digestion must be found by trial and error for every individual emulsion. One method suggested is to make "wet

tests" at frequent periods during the cooking. Suppose, for example, that we are finishing a washed emulsion by digestion in the water bath at 60°C . Every five or ten minutes, a few cubic centimeters can be pipetted from the crock and coated upon a small sheet of glass and set on the ice-cold levelling table. As soon as it is thoroughly set, it is exposed behind a step-wedge (p. 210) for a fixed time and developed for a fixed time at a fixed temperature. The necessary apparatus will of course be available. If the step-wedge be mounted in a deep printing frame, with a thin fillet of wood or aluminum around the edge about a quarter-inch wide, the wet plate can be carefully laid down on the fillet frame and the exposure made without soiling the wedge. Such a test frame should be part of the equipment in every emulsion laboratory. A series of wet tests of this type gives a good visual indication as to when the climax has been reached, by showing more and more steps as the cooking time is extended. After x minutes, when the maximum useful speed has been attained, either fog will step in or the speed will actually diminish, as seen in the series of curves shown in Fig. 23. On future makings, check wet-tests of the emulsion at short intervals when approaching the optimum time of digestion will control the result, though they should not normally be necessary in works practice.

The reader is advised, when making his first negative emulsions, to give the final cooking at 125° to 130°F ., and to coat plates at intervals of ten minutes or so, using a measured amount filtered through one thickness of muslin in a beaker; and to dry these plates in the cupboard, and make strict comparative tests as to speed, gamma, and fog, on the lines discussed in Chapter XII. A suitable coating weight must be made, as otherwise the measure of the fog will be badly out. These tests will furnish information for the guidance of future makings, and provide the best means for investigating any formula, or for checking up a

new sample of gelatin with a known formula. In such tests it is inadvisable to add any finals such as free bromide, alum, preservative or spirit.

It has already been stated that an emulsion comprising grains of a large number of diameters gives the best gradation. It has been frequently recommended that to obtain this quality a mixture of coarse-grained and fine-grained emulsions should be used. If, for example, a very rapid emulsion be made in which a long ripening has brought about the growth of a high proportion of coarse grains having high sensitivity, the admixture of a slower but more contrasty emulsion having finer grain would help to build up highlight density without affecting the shadows appreciably. Jahr⁹ states that highly sensitive but flat emulsions can be mixed in various proportions with contrasty emulsions of medium or even low sensitivity. The addition of a very fine-grain emulsion of high gamma infinity not only helps to increase highlight density, but adds opacity to the mixed emulsion and makes possible a more economical coating weight. On the other hand, it must be borne in mind that when mixing emulsions having a different iodide content, the powerful affinity of iodine for silver may cause some reaction of one emulsion on the other; it is not therefore entirely possible to predict from the characteristic curves of two emulsions that are mixed, exactly what the characteristic curve of the mixture will be.

It is a more reasonable procedure to provide for the precipitation of grains of the various sizes required in one single emulsion, and this can be done by bearing in mind the points which have already been discussed in connection with emulsification. We know, for example, that a concentrated solution of silver nitrate, re-dissolved and "flopped" wholesale into the crock, will give a more or less homogeneous mixing of equal-sized grains producing high contrast with heavy maximum blacks and low

latitude. We know also, that inasmuch as grain size increases with ripening time, the silver could be added in small quantities, spread over a period, so that when the ripening was cut short by the addition of the bulk gelatin, the various precipitates of silver halide would have grown to respectively different sizes. The grain-size frequency curve of an emulsion is an important guide to its characteristics. Owing further to Ostwald ripening, prolonged heating tends to give a maximum of coarse grains, these having grown at the expense of the smaller ones. Hence, by dividing the silver into two, three, or even more parts, and adding them one at a time, it is possible to make an almost unlimited variety of precipitable mixtures providing equally an unlimited variety of characteristics in the finished emulsions.

A further alternative is to add the first silver in the form of a plain, moderately dilute solution (say 1:4 concentration) and after an interval of a minute or two to add the iodide. The remainder of the silver is then added. This tends to increase the time required for ripening, and there is some evidence that the effect of the iodide so added is that of a peptizer, dispersing the initial silver halide precipitate. A variation, therefore, of any formula in which the silver is added in stages, is to add the first silver plain (though some ammonia should be present in the salts solution), then to add the iodide, preferably with a small quantity of ammonia, and finally to add the remainder of the silver in one or more additions. A small quantity of ammonia should always be present in *either* the salts or the first silver solutions, otherwise clots or agglomerates of precipitates may be formed, which will cause black spots on development without exposure, owing to insufficient colloid protection. Silver bromide without a clothing of gelatin will be spontaneously reduced to black metallic silver on treatment with an alkaline developing solution.

Although, with a proper choice of gelatin and a good formula,

maximum speed should be obtainable without fog, several substances have a useful effect in keeping away fog, which really means in destroying the developability of over-ripened or over-digested grains. Thus in his well-known book, *Ausführliches Handbuch der Photographie*, Dr. J. M. Eder gives as substances that destroy latent chemical fog, tincture of iodine, bromine, chlorine, and minute quantities of a dichromate acidulated with mineral acids. Against this, sensitivity is considerably lowered by additions to an emulsion of bromine or iodine, or the metallic perchlorides. The most useful anti-fogging addition is probably a trace of hydrobromic acid, which is frequently made to an orthochromatic emulsion which requires to be fog-free but need not yield any shadow detail, such as for example the so-called document type of emulsion. A few cubic centimeters of a 1:1000 solution of hydrobromic acid may be added to one liter of the emulsion, but its effect should be carefully tested on speed and on the foot of the characteristic curve before such treatment is adopted. A trace of cupric chloride is sometimes used in collodio-bromide emulsions for the same purpose. More recently, anti-fogging substances have been found for use in making extremely high speed emulsions, and thereby making possible some of the newer family of films which have so changed the complexion of modern instantaneous photography; reference to these will be found in Chapter XIV, to which the reader is referred.

The phenomenon of halation, as such, needs little explanation here. While irradiation or reflection of light from the emulsion particles within the film can cause a spreading of the image, the chief trouble is met with in glass plates, where rays of light meeting the film obliquely from the lens strike the far side of the glass support, and are reflected back therefrom, reaching the emulsion again at an appreciable distance from the original point of the image. The application to the back of the support

of an absorbent layer having a refractive index as nearly as possible that of glass, was originally suggested by M. Carey Lea. A later method was to interpose a light-absorbent substratum between the emulsion and the glass or film base. This substratum could be colored with a dye that could be destroyed by an acid fixing bath, or discharged by the use of any one of several other similar treatments which do not at all affect the image.

The idea of employing a light-absorbing film of gelatin containing, for example, curcuma or fuschin, was suggested in 1878. An acid dye would be used, being more readily washed out of the gelatin. As a substitute for a dye, a 0.6 per cent gelatinous solution of potassium permanganate has been suggested by Oakley.¹⁰ The permanganate is reduced during development to more or less colloidal manganese hydroxide which is readily soluble in the average acid fixing bath, or it may be removed by the use of a two per cent solution of sodium bisulphite. Various types of anti-halation treatments are now applied to high speed panchromatic films, for particulars of which the reader is referred to the patent literature. In the case of films, the Eastman Kodak Company has used a magenta dye in the non-curling layer applied to the back of orthochromatic film, and a green layer with certain panchromatic materials. The chemical composition in each case is such that they bleach out completely in a "properly compounded developer and fixing bath." In the case of thirty-five millimeter film, a blue-gray dye is actually incorporated in the base. Light transmitted by the emulsion must thus pass twice through the dye in order to get back to the emulsion and cause halation.¹¹ The blue-gray dye is therefore twice as effective as it would at first appear. It does not bleach out in the processing operation, but its presence has no ill effect on the printing quality.

A further type of fast emulsion which may be dealt with in

this chapter is the reversal film used with many kinds of natural color material. The Autochrome plate, introduced in 1905 by the Lumière Company, gave a positive image in natural colors by means of such an emulsion. The color matrix consists of starch grains colored blue-violet, green, and orange, in predetermined proportions, and on top of this is coated a very thin layer of reversal type emulsion. The plate (or film) is exposed through the back, hence the silver halide grains must be appreciably smaller than the elements of the color matrix. The first development gives a negative image, which is converted by reversal into a positive. The reduced silver is soluble in an acid solution of potassium permanganate or in chromic acid, while the unexposed and therefore unreduced silver bromide is *not*. Hence after "bleaching," the original negative image will disappear, leaving transparent gelatin, while the unexposed silver bromide remains. If, therefore, this be now exposed and developed, it will be in turn reduced and will obviously give black where there was white in the negative image. The negative "blacks" being dissolved out and showing *white* when viewed by transmitted white light, a positive of the original subject is obtained. In the old Agfa color process (The *New Agfa* film is a triple-coated continuous image type, and does not depend upon a matrix. See p. 122) the color matrix, and the matrix and the "reseau" used in Dufaycolor film, are similarly coated with these reversing emulsions. Reversal of this type must not be confounded here with the reversal that occurs in any negative emulsion on gross overexposure, represented in the characteristic curve by the turn of the shoulder where density decreases after a certain maximum of progressive exposure. An exposure of something like one thousand times normal is needed to give a reversed image by straight exposure and development, but such a method is entirely useless for color-screen plates and films.

Owing to the fact that the colored elements of a good matrix for a direct natural-color process must be exceedingly small, the need for an extremely fine-grained emulsion is self-evident; yet it must be fast enough to make snapshot exposures practical. The potato starch grains of the Autochrome matrix, separated out by levigation, vary in diameter between $8\ \mu$ and $20\ \mu$, about four million going to the square inch. The Dufaycolor matrix or reseau has a geometrical formation of alternate lines 500 to the inch, which are dyed red, and lines made up of alternate green and blue rectangles about one-two hundred and fifty thousandths of an inch each in area. The function of the reduced silver grains in any such process is to block out any unwanted color element when the whole image is viewed by transmitted light, or projected. Thus in the case of a green leaf, the image must be transparent only over the green elements, and the blue and red elements must be blocked out by opaque silver deposits. To get this effect as perfectly as possible, the requisite number of grains must be packed into the unwanted area. Yet if the film be too thick or too deep, we may get scatter effects as well as parallax. The desideratum is therefore to have a fast, very finely grained emulsion with such density-giving powers that the thinnest possible coating may be adequate, giving an image as nearly as possible in optical contact with the color matrix. A coating weight determination (p. 231) of an average color-screen film will indicate something between 35 and 65 mg of silver halide per square decimeter — about half that of an average negative film. Even then a developer containing a silver bromide solvent such as a thiocyanate must be used in the first developer in order to get an image of sufficient clarity.

It is by no means certain that we have heard the last of color-matrix types of natural color film. The immense amount of work done by Powrie and others indicates possible success of a highly commercial character, in spite of the success of triple-

coated subtractive films. A very full description of the many lines of attack on the color matrix problem is given in E. J. Wall's "History of Color Photography."¹² Where an emulsion is required for experimental work of this kind, the reader is advised to confine his first attempts to a speed of 200 to 250 H and D. Reference to the hypersensitized emulsions of very high speed will be found in Chapter XIV. An emulsion of the speed named can be super- or hypersensitized after coating by bathing the dry plate or film in a solution of ammonia and alcohol in the proportions:

Distilled water	1000 cc
Stronger ammonia water	3 cc
Alcohol	250 cc

A 0.2 per cent solution of triethanolamine or borax will act similarly, or even soaking in distilled water for three minutes and drying in a warm current of air. Bathed material may be one and one-half to two and one-half times the speed of the original emulsion, but it keeps in good condition for only three or four days, so it must be prepared only slightly in advance of the time when it will actually be needed.

A method of combining initial high speed with fine grain in the reversed image was referred to by the author in 1932.¹³ By using the most sensitive, larger, grains for the exposure of the negative image, and having in the emulsion a sufficiency of small diameter and relatively insensitive grains left over, the latter will, on adequate exposure and development after bleaching out of the initial image, give a reversed image of good resolving power and adequate blocking-out power. Such an emulsion can be made by dividing the silver into two parts, one being re-dissolved and the emulsion ripened, after its addition, in considerable excess of alkaline halide, the other silver being added plain with no ripening time allowed:

84 PHOTOGRAPHIC EMULSION TECHNIQUE

A. Water	2500 cc
Ammonium bromide	380 g
Ammonium iodide	5 g
Soft gelatin	80 g
B. Silver nitrate	300 g
Water	100 cc
Ammonia (s.g. 0.910)	q.s. to redissolve
C. Silver nitrate	300 g
Water to make	1200 cc

Solution *B* is added at 85° F. to the crock containing *A*, which should be at 100° F. After fifteen minutes initial ripening, solution *C* is added through a three to four millimeter nozzle with brisk stirring. The bulk gelatin of 720 g is immediately after added dry, and the whole stirred for fifteen minutes, bringing the temperature up to 105° F. When dissolved, it is set in ice water. After very thorough washing, it is digested for an hour at 125° F. and the color-sensitizing dyes are then added in the usual way. It is finally made up to ten liters with the additions below:

Spirit (less the amount already added in the form of dye solutions)	500 cc
5 per cent chrome alum solution	100 cc
10 per cent phenol solution	100 cc
1 per cent ammonium bromide solution	50 cc

The emulsion is richer in silver than is usual with negative emulsions which are to be used for ordinary photography, but in order to keep the film compact and very thin, only about half the usual coating volume is applied. The gelatin may advantageously be still further reduced if suitable coating facilities exist.

Reversal emulsions are steadily becoming of greater importance. Quite apart from color work, practically all standard motion-picture work is of the reversal type, and im-

mense quantities of 8 mm, 9.5 mm and 16 mm black-and-white reversal films are manufactured. Reversal emulsions are also necessary for triple-layer subtractive color films, and their application is being extended to other purposes where the production of a direct positive image is of advantage. In sub-standard motion-picture work, it is to be remembered that great enlargement of image is involved in projection, so that extremely fine grain is of the utmost importance, always provided that it can be coupled with adequate speed.

Chapter References

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CHAPTER V

SLOW EMULSIONS

Sensitive Material for Copying, Commercial Work and Transparencies — Methods of Producing High Resolution and Fine Grain — Chloro-bromide Emulsions — Chloride Emulsions — Mixed-jet Emulsification — Development of Warm Tones.

IT has been seen in a previous chapter that a fast negative emulsion can be made by "boiling" a suspension of silver bromo-iodide in gelatin until the grains are sufficiently ripened and digested. In this type of emulsion it is probable that sensitization takes place as much in the ripening as in the finishing stage. It has been seen also that by the use of ammonia the temperature and time needed for arriving at a similar speed and character may be greatly modified. It is doubtful whether the extreme speeds attained in recent years can be produced by the boiled method.

We come now to the problem of making comparatively slow emulsions, of 25 to 150 H and D. Such emulsions play a very important part in industry. They are indispensable for copying work, for recording purposes, for the making of transparencies, and for various branches of photo-mechanical reproduction. The coating of positive emulsions on film stock of course runs into enormous figures in the motion-picture industry. Some six thousand million feet of thirty-five millimeter film were used in 1933.¹

In what way, may we ask, do these slow emulsions differ from rapid ones? The answer is that a slow emulsion is made with substantially finer grain, which is not allowed to grow to any extent in ripening. This is controlled by the concentrations of the solutions employed in precipitation, by temperature, and

largely by pH. A slow emulsion may easily be made to develop a gamma of 3.0 or 4.0 and may indeed be required to do so, but it has a fine grain and a high resolution coefficient. The fast emulsion will probably develop a gamma of no higher than 1.0 to 1.8. Apart from improved resolution, irradiation is reduced;

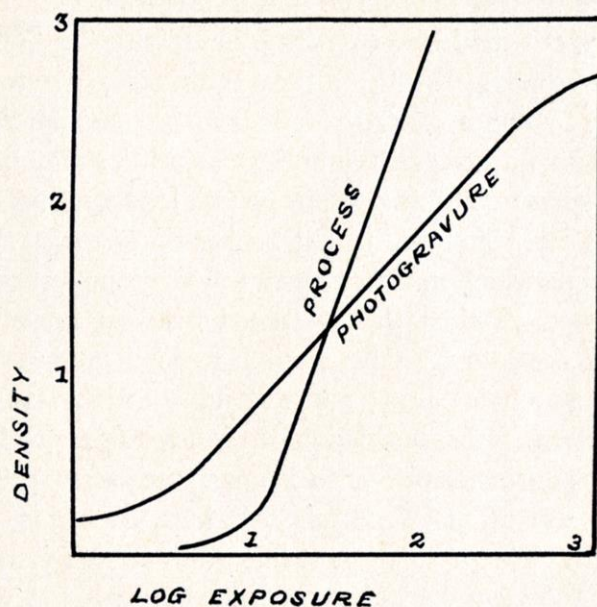


FIG. 24

in other words spreading of fine line images is minimized, and there is a less tendency to halation.

The production of slow, fine-grained emulsions must be divided into two classes, (*a*) the photo-mechanical type, where we need either blacks or whites with no intermediate tones, and a high inertia is of no consequence but rather an advantage, and (*b*) brilliant and contrasty emulsions where the density range is long and latitude is of a high order, but with which high maximum blacks can nevertheless be obtained where desired. The type having a high inertia, and giving intense blacks

on heavy exposures but insignificant densities on low exposures, is seen in characteristic form in Fig. 24, as compared with a transparency type of emulsion having low fog, fairly high maximum density, but a long even scale of gradation. Both types should be made with a high concentration of silver in order that the actual film coating may be as thin as possible.

The first type is made most easily by precipitating the silver halides as far as possible in a uniform grain size. In practice, it is found best to pour concentrated silver nitrate rapidly into the salts solution and to add the bulk gelatin immediately after precipitation so as to inhibit ripening, which is synonymous with grain growth, and also leads to the formation of grains of different diameters, which in turn gives a milder slope to the characteristic curve. Against this, we need brilliant images, low densities and absolute freedom from fog, good gradation and an attainable gamma of 2.0 to 3.0 to provide a first-class transparency emulsion. Our knowledge of the laws of precipitation indicates that pouring the silver in a fine stream with rapid stirring and the use of more viscous solutions, should give the physical result. The production of fine grain needed for photogravure or diapositive work demands not only a more viscous solution for the salts, but reduced silver bromide solvents such as excess alkali halides and ammonia in the ripening. The addition of silver at a moderate concentration or only partially redissolved through a nozzle at a slower rate, with mechanical stirring of the crock, or the pouring of the silver and salts solutions simultaneously through two jets or nozzles into a solution of plain gelatin, gives the "process" character with the longer scale of gradation. Mixed jet emulsions of this type with the whole of the silver redissolved will yield very great contrast, especially if the bulk gelatin be added immediately after precipitation. In very slow emulsions, such as chloro-bromide and chloride types, the substitution of hydrochloric or citric acid

for ammonia is customary, the citric acid often being divided between the salts and the silver.

The following characteristics may be taken as representative of the slower types:

<i>Emulsion</i>	<i>Speed, H & D</i>	<i>Density range</i>	<i>Gamma infinity</i>
Photogravure	60-100	1.5	1.8
Process	25-60	2-3.5	3-5
Lantern	6-10	2.5	3
Chloro-bromide	1-2	2.5	2
Chloride	0.1-1	4	4

It has already been pointed out that the characteristic curve is steepened and latitude shortened by having more or less homogeneous grains of similar diameter. This condition is obtained in the formula given below by adding a concentrated redissolved silver at a low temperature to the salts, adding the gelatin at once and setting as quickly as possible. Alternatively the salts and silver can each be dissolved in the same bulk of water and poured into the crock simultaneously with the apparatus described on p. 100. The gelatin solution may be made alkaline with ammonia, or acid with a mineral acid to neutralize the ammonia set free by reaction of the silver nitrate with the alkaline halides. This helps control the tendency for rise in speed.

Bearing in mind that a process emulsion when coated requires about sixty to eighty milligrams of silver halide per square decimeter, and that the gelatin-silver ratio should be kept low, we may formulate the emulsion somewhat as follows:

A. Ammonium bromide	230 g
Ammonium iodide	5 g
Gelatin	200 g
Water	4000 cc
B. Silver nitrate	350 g
Water	50 cc
Stronger ammonia water	q.s. to redissolve

The gelatin is soaked for thirty minutes in the salts solution *A*, which is then heated and the gelatin dissolved. It is then cooled to 95° F. (35° C.). Solution *B* is used at room temperature, 70° F. (21° C.), and is poured on quickly out of a stoneware jug, taking two or three seconds only. The crock should be vigorously stirred, if possible by mechanical means. Immediately after emulsification, 550 g of powder or broken gelatin is added, the jar being stood in water at about 160° F. (70° C.) to facilitate quick melting, but the temperature of the emulsion itself must not be allowed to rise above 105° F. (40.5° C.). The gelatin will take ten to fifteen minutes to dissolve completely. The emulsion should then be transferred to an ice-cold crock or a number of smaller ones and stood in ice water, stirring until gelling begins. Not more than three to four hours should be allowed between setting and washing. The final wash water should give a clean Nessler test. When washed, 250 cc of spirit is poured over the shreds, which are then remelted in the usual way, and the emulsion is digested for about two hours at 125° F. (52° C.). One or two cubic centimeters of ten per cent glacial acetic acid solution is added and well stirred in, sufficient to bring the pH to just below 7. The remainder of the alcohol, 250 cc, is then added, together with 100 cc of chrome alum solution and 50 cc of ten per cent potassium bromide solution. The emulsion is next filtered and set off, being remelted next day or when required for use. Such an emulsion will keep in the cold room for several days, but should always be checked for fog by a wet test before being sent to the coating room. The total bulk of the above emulsion should be ten liters.

The wet test for fog is made by coating about twelve cubic centimeters of the emulsion on a 5 by 7 inch plate, setting it on the cold slab, and placing it in a plateholder with the slide half drawn. It is exposed about eight feet from a 25-watt in-

candescent lamp for a few seconds, and then washed under the tap and developed in total darkness for about three minutes in any ordinary M.Q. developer. The exposed portion will develop up jet black, and the unexposed part should appear by comparison dead white in the Mazda light.

E. J. Wall gives the following formula for a process emulsion:

A. Potassium bromide	450 g
Potassium iodide	5 g
Gelatin	625 g
Water	4800 cc
B. Silver nitrate	500 g
Water	1250 cc
Ammonia to redissolve	

Solution *B* is run into the salts solution through a very fine jet, taking fifteen minutes. *A* is at 68° F. (20° C.), and *B* at 113° F. (45° C.). The mixed emulsion is then digested for fifteen to thirty minutes, cooled, set and washed, and finished in the usual way. Note that the viscosity of the salts solution is quite high. Jahr suggests at least doubling the gelatin used in emulsifying an ordinary type emulsion and increasing the iodide by fifty per cent. It is the author's experience that an iodide content of not more than 1.5 per cent of the silver nitrate equivalent, a considerably lower concentration of the gelatin in the jar (about four per cent), and a very concentrated silver solution, give the best grain and contrast for photo-mechanical emulsions, provided always that the addition of the bulk gelatin and the setting be *very quick*.

When we come to plates or films suitable for photogravure, where a density range of not more than 1.5 is required, and a maximum density of say 1.8 (the lowest tones having a density of 0.3), a somewhat modified type of emulsion is needed, involving a longer scale of gradation and lower gamma infinity. This may be obtained in two ways. Either fifty per cent only

of the silver may be redissolved and the remainder added plain to the salts five to ten minutes after the first precipitation, and ten to twenty minutes allowed for ripening, or a portion of the silver nitrate solution, say one third, may be first added dilute to the salts, with the iodide omitted. Instead of redissolving this first silver nitrate, about one third only of the amount of ammonia that would be required to redissolve it, should be added. This will, of course, give a dirty brownish black solution containing undissolved silver hydroxide, but this will not disturb the result. On emulsification it will yield a perfect silver bromide precipitate. After an interval of, say, three minutes, the iodide is added in about ten times its weight of water, rendered alkaline by ammonia to about five per cent of the total weight of silver; immediately afterwards the balance of silver is added plain, at a temperature of 115° to 120° F. Ten to fifteen minutes further ripening may then be given, and the bulk gelatin added. The formula would thus appear as follows:

A. Ammonium bromide	230 g
Gelatin	160 g
Water	2600 cc
Temperature 110° F.	
B. Silver nitrate	120 g
Water to	440 cc
Stronger ammonia water	40 cc
Temperature 70° F.	
C. Ammonium iodide	6 g
Water	60 cc
Ammonia	18 cc
Temperature 70° F.	
D. Silver nitrate	240 g
Water to	960 cc
Temperature 120° F.	
E. Dry gelatin	640 g

In coating emulsions for photo-mechanical work, it must be borne in mind that the thinnest possible film should be made which is sufficiently robust. A considerable amount of handling takes place in processing, and while the film must exhibit no tendency to frilling and must be abrasion-proof, it must be thin enough to make the various operations such as cutting with ferricyanide, intensifying, washing, etc., as quick as possible. The addition of a yellow dye such as Brilliant Yellow, Tartrazin, or Naphthol Orange, will assist in preventing spreading of the image by irradiation. Some form of backing is, however, the most satisfactory means of preventing halation.

The slow photo-mechanical emulsions above described range in speed from 25 to 150 H and D. A still slower type is used for black tone diapositive and lantern plates. A speed of 5 H and D is very suitable for lantern emulsions, and here again absolute freedom from fog is most important, as it greatly enhances brilliance on projection on the lantern screen.

The formula below is stated to yield excellent slow iodobromide emulsions for transparencies:

A. Potassium bromide	150 g
Potassium iodide	4 g
Gelatin	250 g
Water	2500 cc
B. Silver nitrate	375 g
Water to	2500 cc

One cubic centimeter of five per cent pure hydrochloric acid is added to A. Both silver and crock are heated to 130° F. (55° C.) and emulsified. The crock is stirred and maintained at 140° F. (60° C.) for thirty minutes. Then add 300 g of dry gelatin and dissolve with stirring. The emulsion is then set off in ice water. While the addition of a little ammonia to the emulsion is suggested just before setting, such procedure is *not* recommended by the author. The washed emulsion, after the

addition and solution of another 250 g of dry gelatin, must be digested at 120° F. (49° C.) for a time varying from an hour and one-half to three hours. This time depends largely on the brand of gelatin used, and can be decided only by actual test. The usual procedure is to take samples periodically from the crock as it stands in the digesting pan, and coat sample plates, making sensitometric tests of the series of plates when *dry* under identical conditions of exposure and development. Finals are:

Spirit	500 cc
5 per cent chrome alum solution	50 cc
10 per cent potassium bromide solution	50 cc

As a preservative in this or any slow emulsion, there is little to beat carbolic acid (phenol), of which about three grams to the gallon may safely be used. This may be dissolved in the spirit, except where the spirit is poured on the shreds in remelting them after washing. The final bulk of the above emulsion prior to filtering should be 12,500 cc.

Reference to the literature will disclose many formulas in which the gelatin is divided equally between the salts and the silver, thus mixing two viscous solutions in the precipitation. While an extremely fine grain can be obtained in this way, it is not easy to avoid grain aggregates, which give black "pepper" spots in the developed image. Preferable to the divided-gelatin method is the double-jet method of precipitation described later.

A slow emulsion made with a mixture of the chloride and bromide of silver has the property of yielding warm black, sepia, or reddish-brown tones, on straight development, and has therefore been much used for transparency and lantern slide work. Similar emulsions applied to paper give warm black tones which have been much in vogue. These tones are to be distinguished from the tinted images obtained by the use of motion picture positive stock coated on slightly tinted nitrate base.

The ratio of bromide to chloride is capable of infinite variation, affecting both contrast and color, although the physical formation of the halide grains can equally influence both the tone formed on straight development and the effect on tone of restrained or diluted developers. Just as the higher affinity of iodine for silver over that of bromine will cause an iodide to turn out some of the bromine of silver bromide, so a bromide will convert some of the chloride of silver into bromide or bromochloride. If the bromide be much in excess of the chloride in an emulsion in which both halides are present, the tone will be colder but the gradation will usually have a longer scale; an excess of the chloride will tend towards higher contrast and a shorter scale, but will more readily yield color on suitable development.

A point noticeable in the study of published formulas is that in these emulsions a very small excess only of soluble halide over the combining weight is employed, and that free acid, often in considerable quantities, is used. This will be seen from the two following formulas, due respectively to J. B. B. Wellington and E. Valenta:

	<i>Wellington</i>	<i>Valenta</i> ^{÷ 10}
A. Ammonium bromide	20 g	2.0 g
Ammonium chloride	—	11.6 g
Sodium chloride	10 g	—
Citric acid	50 g	—
10% nitric acid	—	4 cc
Gelatin	70 g	65 g
Water	500 cc	500 cc
B. Silver nitrate	50 g	50 g
Citric acid	50 g	—
Water	500 cc	500 cc

The method of mixing varies. In Wellington's formula, the silver solution is introduced in a fine stream at room temperature to the salts solution, which has been heated to 160° F.

(70° C.). The emulsion is allowed to stand for ten minutes and is then set and washed. Valenta on the other hand recommends heating both salts and silver solutions to 140° F. (60° C.) and adding silver to salts in the usual way.

Another formula, due to Valenta, and suggested for transparency work, is quoted by Jahr: ²

A. Ammonium bromide	15.2 g
Sodium chloride	1.5 g
Gelatin	50 g
Water	400 cc
B. Silver nitrate	30 g
Water	400 cc

Both solutions are heated to 140° F. for emulsification, and after mixing, the jar is maintained for an hour at 140° F., being mechanically stirred during this time. It is then set and washed.

It will be noted that after washing, these emulsions have a rather low gelatin concentration. Chloro-bromide and chloride plates should have a very thin film of emulsion and a coating weight of not more than twenty-five to forty milligrams of silver halide per square decimeter. If difficulty is experienced in coating in the laboratory, a little fresh gelatin may be added to the washed emulsion on remelting, bringing the gelatin up to about six per cent of the total weight of liquid. It must be very thoroughly dissolved by stirring, solution being complete before adding the alcohol and chrome alum. It is usual to reset the emulsion after making up and to remelt just before filtering, prior to coating. Little if any free bromide should be added; a small excess of chloride may be beneficial, although it may impart a greenish tint to the blacks, or be prejudicial to warm brown tones by imparting to them a greenish tinge. This green tinge is particularly difficult to eliminate in chloro-bromide papers. If there is a tendency to fog, or if the image is too flat, a little potassium chloride solution may be used, together with

a little citric acid, not potassium citrate. Better still is a change of gelatin. Most manufacturers are aware of the particular types of gelatin which suit these slow emulsions, and will provide likely samples if asked.

Potassium chloride is suggested rather than sodium or ammonium chloride, as it is not hygroscopic, and hence can be used even with an unwashed emulsion. It will be noted that the chlorides and bromides of various alkali metals are used in different formulas, but experience has proven that provided the respective combining weights are employed they all work much alike. This does not apply to metallic salts such as cupric chloride and thallium chloride. The use of one to three per cent of cupric chloride (compared with the silver) can perceptibly increase the brilliance, tending to give improved whites and better contrast in projected screen images. Cupric chloride solution is added to the finished emulsion when making up.

The gelatin being at high concentration in emulsifying and there being practically no excess of soluble halides and a low pH, little ripening takes place, hence the grains remain small and any tendency toward speed is inhibited. According to Jones,³ redness of the image, i.e., its departure from *black*, is dependent on the size of the developed grains. This was well illustrated by the work of L. F. Davidson and T. T. Baker on the photomicrography of developed chloro-bromide images using a $\frac{1}{20}$ -inch oil immersion lens (Beck) and dark ground illumination, with Agfa color plates. The color of the grains by transmitted light was excellently recorded. Warmth of tone is best regulated by length of time of reduction coupled with the presence in the developer of a small trace of silver halide solvent. The particular type of fine-grained emulsion containing chloride in conjunction with bromide of silver seems to lend itself to the production by direct development of colloidal silver of ultra-microscopic size, yellow, red, or purple grains being re-

duced with a proportion of black grains of microscopic size. The presence in the developer of ammonium chloride or ammonium carbonate definitely helps the formation of color, but these compounds can only help when the grain size is of a suitable fineness. Apart from the actual *size* of the silver halide precipitate, the use of more concentrated gelatin in emulsification gives a more solid clothing of the particles, which again appears to assist in the production of color. In the case of pure chloride emulsions (*q.v.*) it is noteworthy that a plain hydroquinone-caustic soda solution, or a developer such as the Gevaert G-251, will yield most easily a series of tones from warm black to red merely by *dilution*, giving longer development time with exposure remaining more or less constant. Several hours' development with extremely dilute hydroquinone-soda can be made to yield purple and bright magenta tones.

Silver chloride darkens in the light, but will yield only a flat, grayish image on prolonged exposure.* Given an exposure under a negative of the order of 25,000 meter-candle-seconds, which may or may not give rise to a faint visible image, the emulsion can be developed to an intense blue-black in any suitable solution such as amidol or metol-hydroquinone. Silver chloride is, in general, emulsified with gelatin by adding silver nitrate to the solution of chloride, though the pouring of the gelatin-salts solution on to the silver solution has been advocated. The gelatin is sometimes dissolved in the salts solution, sometimes divided between the silver solution and the salts solution. Another favorite method is to run solutions of silver nitrate and sodium, potassium, or ammonium chloride through

* If a small quantity of potassium or sodium nitrite be added to a silver chloride emulsion, it will "print out" in sunlight and give an image of sufficient depth to be toned with gold and fixed. Exposure-meter paper is usually prepared with a nitrite to induce visible darkening of the silver halide.

two matched jets into a plain solution of gelatin, the salts being always very slightly in excess. This method has the advantage that the silver chloride is not formed initially in a large excess of soluble chloride, which excess diminishes progressively as the precipitation proceeds, but the conditions of colloidal precipitation are maintained constant through the entire emulsification.

One essential of a chloride transparency or development paper is that the whites must remain absolutely clean, that is, that the fog density on normal development does not exceed about 0.02. Another is that the blacks are bluish black or warm black, but are not greenish in tone. These features are mentioned because it is by no means easy to insure them. Also, as with all slow emulsions, it is not always easy to obtain sufficient contrast. A gamma of 4.00 or thereabouts should be one of the features of a chloride emulsion. One difficulty in the making of the emulsion is the avoidance of coarse precipitates, which develop spontaneously owing to insufficient colloidal protection; these cause the black spots or flocks previously referred to as pepper, and may easily spoil an otherwise good emulsion.* Their formation appears to be quite independent of the concentration of gelatin or rate of stirring, but it is always a liability where the chloride of silver is concerned. A suitable coating weight is twenty to twenty-five grams of silver chloride per liter, one liter being allotted to a twenty-foot run of paper forty-two inches wide or the equivalent of four hundred lantern plates 3 by $4\frac{1}{4}$ inches.

Many formulas have been published for fine-grain, slow emulsions, particularly chloride and chloro-bromide, in which the

* A certain amount of small flocks has been found an actual advantage in emulsions for photogravure. Their formation appears to rob the blacks of some of their density, thereby making them more transparent and assisting shadow detail, while not interfering perceptibly with highlight detail.

100 PHOTOGRAPHIC EMULSION TECHNIQUE

salts and silver solutions are poured simultaneously into the crock containing plain gelatin solution. The silver halide is then formed throughout the precipitation with a constant excess of salts, which can be adjusted to be extremely small, and can be controlled by the time of lead given. Thus in Fig. 25

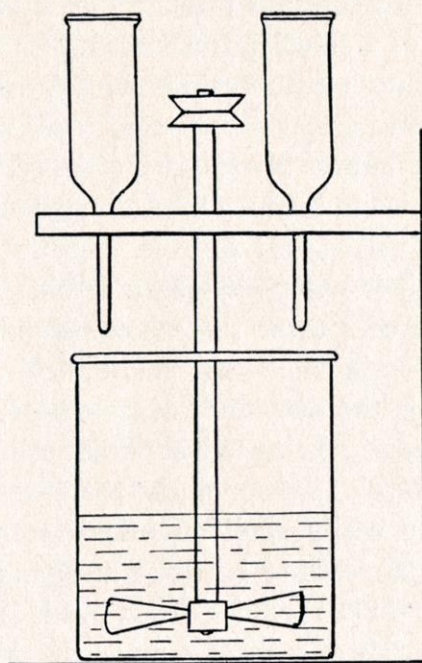


FIG. 25

the two solutions are poured into two cylindrical funnels the ends of which have been drawn out in the flame into fine jets. By making the drawn-out part long enough (Fig. 26) small bits can be filed and broken off in different positions as indicated by the arrows until the cylinders empty at the same rate. Another method is to connect a short length of barometer tubing, say one inch long, to the outlet of the funnel by a piece of rubber tubing; in this way tubes of the same bore can be assured, and the salts merely started, with a pinchcock, so many seconds be-

fore the silver. Any timing must of course be made with samples of the actual solutions to be used, each at its respective temperature. It is not advisable to use funnels with glass taps. If, say, 2000 cc each of silver and salts are to be poured into

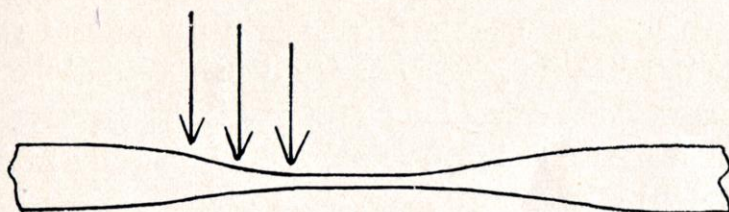


FIG. 26

5000 cc of ten per cent gelatin solution, 25 to 50 cc of the salts solution would be run in before the silver was started. This would insure a lead of halide and prevent free silver nitrate from coming into contact with the gelatin, which might give rise to dichroic fog or veiling.

Mixing of this type, as a rule requires vigorous stirring. This may be done by means of a glass, wooden, nickel, or chromium-plated propeller, or a pair of propellers running in opposite directions. Small variable laboratory stirrers are supplied by Eimer and Amend and Central Scientific Company; these are fitted with induction motors so that no sparking takes place. It will be found, however, that for quantities of two liters upwards, with viscous solutions of gelatin, considerable power is required to insure efficient continuous stirring. With sufficient practice the hand and wrist and a one-half or three-quarter inch stirring rod are difficult to beat for experimental lots of a liter or two. But where a series of strictly comparative tests is being made, proper control and uniformity of mixing is naturally essential. In works practice a one-half-h.p. motor would have sufficient power for stirring a crock of three gallons capacity or more.

It must be borne in mind that starting with 5000 cc of ten per cent gelatin solution, the gelatin concentration in the crock at the end of mixing will have dropped to 5.5 per cent. If uniform concentration is to be maintained, then if x per cent of gelatin be used in the water in the crock, the silver and salts solutions must each contain x per cent of gelatin also; in this case the gelatin concentration of each of the three solutions would be reduced to 5.5 per cent in the above example. Further reference to this type of emulsification will be found in Chapter VIII.

Care must be taken in the drying of transparency plates, as owing to the thinness of coating, drying marks at the edges are apt to appear. The rate of drying is limited by the rate of diffusion of water in the gelatin layer to the evaporating surface; ⁴ it thus progresses more rapidly at corners and edges and proceeds by a gradual regression of the moist area to the center of the plate or film. It would appear that the extra tension due to the more rapid drying renders the sensitive salts liable to darken on development without exposure (*cf.* pressure marks), and to prevent the trouble with thinly coated slow plates, it will be found advisable not to turn the heat on in the drying cupboards as soon as in the case of thicker-coated bromide plates. An addition of one-quarter per cent of glycerin to the emulsion may be found helpful.

Chapter References

1. Twentieth Century Fox Film Report, 1933.
2. R. Jahr, *Handbuch der Wiss. und Angew. Phot.*, p. 240.
3. Chapman Jones, *Phot. J.* 51, pp. 159-174.
4. *Photography as a Scientific Implement*, p. 139.

CHAPTER VI

COLOR-SENSITIVE EMULSIONS

Action of Color-Sensitizers — Orthochromatic and Panchromatic Plates and Films — Self-filtering Emulsions — Hyper-sensitizers — Bipacks and Tripacks — Three-layer Color Films — Dye-couplers and Color Formers

A PLAIN silver iodo-bromide emulsion is not sensitive to color as is the human eye. The maximum response is to light of wavelengths ranging from 430 to 470 $m\mu$ in the blue-violet, the sensitivity ending at about 520 $m\mu$ in the green region of the spectrum. Ordinary emulsions are sensitive to the extreme violet and ultra-violet, response to the latter being terminated by the ultra-violet absorption of gelatin. By reducing the gelatin to a minimum, the response can be lengthened to about 180 $m\mu$. Silver bromide emulsions are also sensitive to the shorter radiations having wavelengths varying from 10^{-9} to 10^{-7} cm, and even to the gamma rays, which are of the order of 10^{-8} mm.

The response of a gelatino-bromide emulsion to the spectrum of white (incandescent) light is seen in *E* in Fig. 27; the visual activity *V* is shown in comparison with it. It is seen that while the most active color visually is situated at about 555 $m\mu$, the bromide emulsion has a maximum response at a much shorter wavelength. The relative sensitivity of average "ordinary" or "color-blind" emulsions, orthochromatic (green-sensitive), and panchromatic (fully color-sensitized) types is seen compared in Fig. 28, the green-sensitive type (*B*) having a characteristic hump at 540 to 550 $m\mu$, and the panchromatic (*C*) having — usually — two less clearly defined maxima at 540 and 640 $m\mu$, indicating the use of two color-sensitizers. Combina-

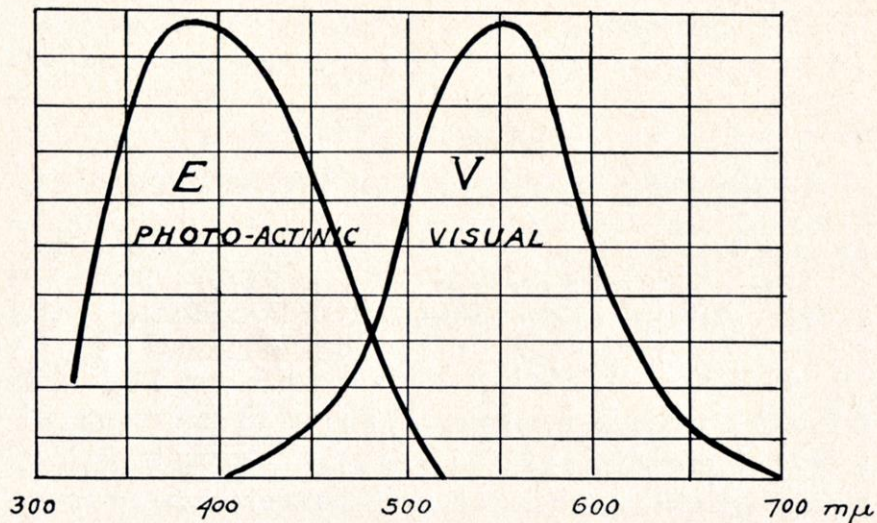


FIG. 27

tions of color-sensitizers have been found which together produce an almost continuous response without appreciable maxima from the violet to the middle red of the spectrum.

Color-sensitizers are dyes which when added to the emulsion actually color the silver halide grains or their sensitive nuclei or spots so that they absorb additional radiations, the energy of which can be converted into chemical energy and thus render the grains reducible in the developer after exposure. As the photo-chemical reaction when light impresses the film can only take place if the radiations are absorbed by the system, it can be understood that the dye used must be complementary in color to the rays for which it "sensitizes." The maximum of sensitivity conferred does not, however, coincide exactly with the absorption maximum of the dye, but in the case of iodobromide emulsions is generally shifted 15 to 20 mμ towards the red end of the spectrum. This shift is complicated by the fact that the dye may impart to the grains a different color from its own in aqueous solution, and that it may color silver bromide,

silver chloride, and silver iodide, differently among themselves. An important desideratum in color-sensitizing is to provide as far as possible that no excess of dye is used over and above that actually needed to give the optimum result in any particular emulsion.

For many years after the possibility of color-sensitizing had been discovered, only greenish-yellow sensitivity could be added to the normal blue-violet response. This was done by adding the dye *eosin* to the emulsion, first suggested by Waterhouse and afterwards used successfully with collodion by Vogel. Tailfer later used eosin and erythrosin in conjunction with ammonia in making gelatino-bromide plates. Erythrosin is one of the finest green sensitizers available even today, and is an alkali salt of fluorescein (potassium or sodium tetra-iododofluoresceinate). It stains the grains pink or magenta, so that they absorb light of the complementary color *green*; the dyed emulsion is thus sensitive to violet, blue and green. The increased truthfulness of the monochrome rendering of colored objects with these plates caused them to be named orthochromatic or isochromatic. Wall states¹ that from 0.07 to 0.10 gram of the potassium salt is generally used to one hundred grams of silver nitrate.

In the first years of the present century, fairly powerful yellow and red sensitizers were discovered, and thus it became possible to render an emulsion sensitive to the entire range of the

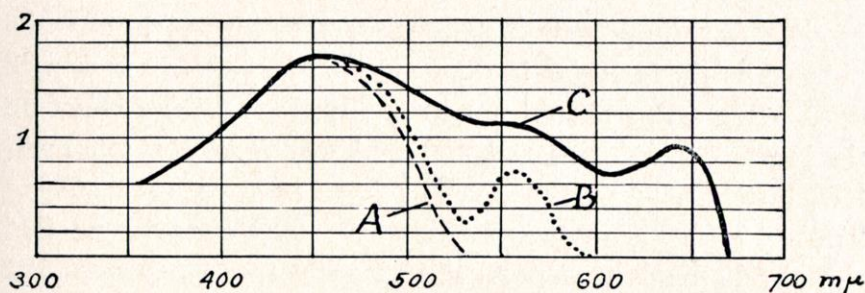


FIG. 28

visible spectrum. Such emulsions were termed *panchromatic*. It must be noted, however, that comparatively few dyes will act as color-sensitizers, and that these require to be used in the highest possible state of purity if consistent results are to be obtained.

Two things will be noticed from a consideration of Figs. 27 and 28. The visual and photographic curves of Fig. 27 are similar in shape but considerably displaced as to wavelength. Fig. 28 shows that while the blue-violet sensitivity *A* remains in each type of emulsion, neither the ortho *B* nor the panchromatic variety *C* has anything like the response of the human eye to the other colors. Color-sensitive plates, from the emulsion maker's standpoint, must therefore be divided into three distinct classes:

- (a) The orthochromatic type, suitable for general landscape and flower photography, document work, etc., when used with a yellow filter on the lens to depress the predominant blue-violet sensitiveness.
- (b) The panchromatic type, more or less evenly sensitized to all visible colors from 400 to about 650 $m\mu$, required for black-and-white reproduction of colored objects fully corrected, or for color photography where the spectrum is divided into three more or less equal parts, blue-violet, green and orange-red.
- (c) Locally sensitized types, with sharp peaks of color-sensitiveness, of special value in conjunction with contrast filters for photomicrography or for regional spectrography and other scientific purposes; in this category infrared plates would be included.

In class (a) the predominant sensitivity to blue-violet may be reduced by the inclusion in the emulsion of a yellow "filtering" dye. Such a dye should not have any desensitizing effect on the intrinsic speed of the silver bromide grains. Naphthol yellow, tartrazin and thiazol yellow have been recommended;² brilliant yellow is another suitable dye. The filter-dye method can also be made to depress the blue-violet in a panchromatic emulsion to make it have a color response similar to curve *V*

in Fig. 27, but by some curious mischance this has never been offered to the public by manufacturers, who appear to find the panchromatic film plus compensating filter more practical. An emulsion which gave remarkably good monochrome rendering of colored objects without a filter was that in which F. F. Renwick used auramin,³ which he claimed not only acted as a blue sensitizer but increased the range of sensitivity in the red obtained with pinacyanol; the auramin actually depressed violet and made a partial self-screening, though this is not claimed.

The green sensitizer used in the most popular orthochromatic emulsions is undoubtedly erythrosin (Fig. 29). It is largely

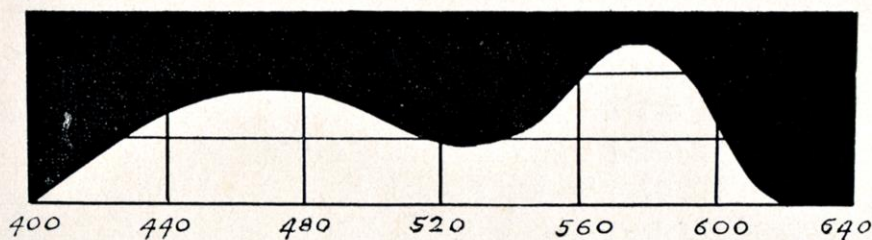


FIG. 29

employed in the industry for plates, films, and document papers, and is used in many rollfilm emulsions where it confers mild green sensitivity and increases brilliance. It gives little color correction in daylight unless used with a yellow filter. Erythrosin can be added to a finished emulsion or it may be mixed with the silver solution just before emulsification. Eder's early formula, which has never been greatly improved, involved the addition of a solution of erythrosin to the ammonia-redissolved silver; this procedure probably gives the highest peak of green sensitivity that can be obtained. The addition to a finished emulsion of a solution of erythrosin containing a small quantity of ammoniacal silver hydroxide or a weak solution of silver chloride in ammonia, may give extremely pronounced green

108 PHOTOGRAPHIC EMULSION TECHNIQUE

sensitivity, but is likely to cause fog, poor keeping, and black spots, and is only advised where a very pronounced peak is desired for special work.

The following emulsion, based on Eder's lines, will be found very satisfactory:

A. Water	3500 cc
Ammonium bromide	350 g
Ammonium iodide	8 g
Soft gelatin	150 g
B. Silver nitrate	500 g
Water	250 cc
Ammonia, concentrated	to re-dissolve
Just before mixing, add two per cent erythrosin, dissolved in equal parts of alcohol and water 25 cc.	

0 drop

Using the salts solution at 90° F. and the silver at 70° F., the silver is "flopped" into the crock without stirring. When added, it is stirred gently for one minute. Six hundred and fifty grams of dry gelatin is then added and stirred in for fifteen minutes, bringing the temperature of the crock up to 105° F. It is then set quickly in ice water, very thoroughly washed after about five hours, and digested as usual. Final volume to be ten liters, inclusive of:

13

5 per cent chrome alum solution	100 cc
5 per cent phenol in alcohol	500 cc
1 per cent ammonium bromide solution	50 cc

If the emulsion is to be made self-screening, there should be introduced *before* the finals sufficient of the yellow dye in a watery solution of about two per cent strength to impart a pale yellow color to the emulsion when tried out on glass coated with about the normal thickness, 10 or 12 cc to a 5 by 7 plate. A number of trials must of course be made, and tried out when dry by photographing a color chart in daylight or daylight-filtered Mazda without a compensating filter. Loss of speed

may be due to the presence of a " filler " in the dye, or to the use of too large a quantity of dye, or to insufficient green sensitivity to admit of the use of the filtering dye. Pure dyes must be used for this purpose.

Erythrosin for emulsion-making purposes is made of exceptional purity by Meister, Lucius and Brüning of Hoechst am Main, Germany. A pure grade is also supplied by Eastman Kodak Company (product of National Anilin Company). Commercial erythrosin may be purified, according to Wall,⁴ by dissolving three parts of the dye in one hundred parts of water, and adding dilute sulphuric acid gradually until the whole of the tetra-iodo compound is precipitated, the solution being then colorless. The precipitated dye is filtered off and washed repeatedly with distilled water. It may then be conveniently made up as a two per cent solution, dissolving it in a mixture of equal parts of distilled water and alcohol, to which a few drops of ammonia have been added. Instead of adding the erythrosin to the ammoniacal silver solution, this dye solution may be added, as stated, to the finished emulsion, in which case the quantity employed would be the equivalent of about one part of solid dye to one thousand parts of silver halide. It is best added five or ten minutes before the end of the final digestion. It must be remembered that any emulsion sensitized for greenish-yellow must be handled in deep red light. Both emulsion and coated plates should be shielded from direct rays, and the safelights should be re-tested from time to time.

While there may be nothing to replace the old erythrosin as an all-round green sensitizer, Meister, Lucius and Brüning have produced *pinaflavol*, which confers extraordinary sensitivity in the blue-green, continuing through to the beginning of the yellow. It appears to show a tendency with some emulsions to give fog, and a somewhat low gamma. It is a basic dye, and the fact that it produces a response to the most obstinate part

of the spectrum, the blue-green region around 520 m μ , makes it of particular interest. The pinaflavol maximum is, in fact, at about 527 to 530 m μ . For adding to a finished emulsion, the makers recommend the use of about 20 cc of a 1:1000 solution to the liter. Both Orthochrom T and pinaverdol are recommended, but while excellent green sensitizers, they confer such high orange and red sensitiveness that they should be considered along with the panchromatic dyes.

The use of too much dye is liable to cause fog, does *not* increase color-sensitivity, and may slow the emulsion by deeply coloring the grains and the surrounding gelatin, thereby acting as a light-filter rather than as a sensitizer. This point is well illustrated by the increase in sensitivity which can be produced by merely bathing commercial panchromatic plates in plain water.

The next type of dyes to be considered comprises the derivatives of quinoline, such as cyanin itself, the iso-cyanins introduced by Miethe, and the carbo-cyanins more recently applied by König. An immense number of these sensitizers has been produced and investigated in recent years. It is beyond the scope of this book to enter into the chemistry of these compounds, and for their study the reader is referred to the last few years' issues of "Photographic Abstracts," published quarterly by the Royal Photographic Society of Great Britain, and the library of the U. S. Patent Office, where a vast and constantly growing number of patents are available. Practically every important manufacturer of films and plates today possesses his own organic laboratory for the manufacture of his sensitizers. A few of these have been placed on the market, but the firms concerned have not been over generous, and the cream of such products are not only reserved for factory production, but their use is hedged around by the patent position.

The great increase in speed of panchromatic emulsions wit-

nessed in recent years has been largely due to the new technique of "super-sensitization." That it is possible to attain sensitization by the addition of such super-sensitizers higher than the sum total of the individual sensitizers, is claimed by Dr. C. E. K. Mees.⁵ An alcoholic solution of the sensitizer and super-sensitizer is diluted with water and added to the emulsion. As a given instance, ten parts of pinacyanol may be super-sensitized with one part of pinaflavol, the region of response induced by each, overlapping. The net effect is to obtain greater speed in the sensitized region than the sum of the two sensitivities conferred by each separately. Another example is that of a thiocarbocyanin, super-sensitized by the addition of 8-alkyl-diabenzthiocarbocyanin.

The amount of these color-sensitizers added to an emulsion is small as compared with fluorescein salts. About 0.05 per cent of the weight of silver bromide would be used in the case of pinacyanol; 0.07 per cent in the case of pinachrome, Orthochrom T or pinaverdol. These dyes are all rapidly decolorized on exposure to light in the form of aqueous solutions or thin films. The color-sensitiveness they impart is retarded by the presence of free bromide in the emulsion, which appears to oppose the dyeing of the halide grains. This is probably the reason why the addition of a trace of silver nitrate to the sensitizing bath often increases the effect, but such addition is dangerous practice unless the washing of the emulsion is made under the strictest possible control.

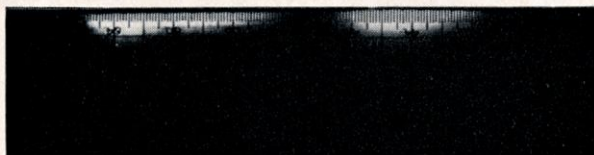
Some of the modern red-sensitizers give the best results if added to the emulsion before it is completely digested, this seeming to assist in the adsorption of the dye on the halide grains or their nuclei. Whether the emulsion is digested with the dye in, or the dye is added at the final stage, it is important that it should be absolutely free from fog — one for example which will give on normal development without exposure, a fog read-

ing of not more than 0.02. For the reason already noted, the smallest possible quantity of free bromide should be added as a final, and extra careful washing should be given to insure that the excess bromide used in emulsification is thoroughly removed. Lithium bromide is sometimes recommended as giving cleaner results than the potassium salt. An emulsion having a low iodide content, say two per cent only of the silver bromide, also reacts in general more favorably to the sensitizers. Owing to their fugitive character the isocyanins and analogous dyes should be made up in artificial light and stored in dark bottles. A warm mixture of ethyl and methyl alcohol is generally used to dissolve the dye, which is as a rule soluble only about one part in a thousand (1:5000 in the case of Sensitol Violet), and when dissolved the solution is broken down to strength by further addition of alcohol. Where two or more sensitizers are used, it is advisable to add each one separately, with a short interval between additions.

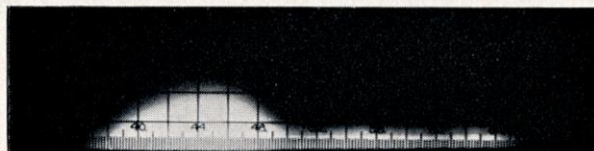
Different sensitizers must be used in different quantities to produce the best results. In the majority of cases the spectral band or bands for which the dye sensitizes is not interfered with by the next dye added. Thus it is claimed that pinaflavol, used to sensitize up to 590 m μ with a maximum at 527 m μ , can be used with pinacyanol, which will continue the sensitivity along the spectrum up to about 640 m μ . By a combination of dyes the peaks of which, as measured on a wedge spectrograph (p. 210), add up to a more or less uniform level, it is possible to produce a panchromatic emulsion having almost equal sensitivity throughout the visible spectrum.

For many cases of scientific work, it is of advantage to use plates or films locally sensitized; thus eosin, erythrosin, rhodamin, etc., give a pronounced green maximum and can be used with good results in conjunction with a green contrast filter in the photomicrography of specimens stained with carbol fuch-

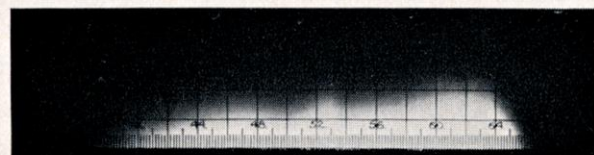
Violet Blue Green Orange Red



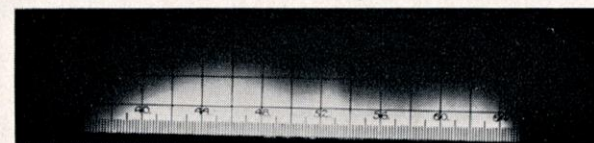
PANCHROMATIC TYPE A (Tungsten)



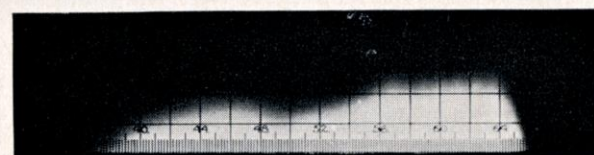
PANCHROMATIC TYPE A (Daylight)



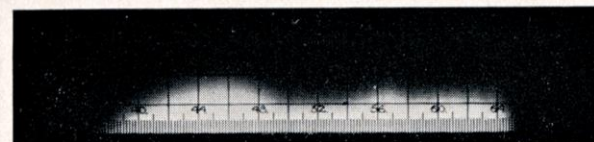
PANCHROMATIC TYPE B (Tungsten)



PANCHROMATIC TYPE B (Daylight)



PANCHROMATIC TYPE C (Tungsten)



PANCHROMATIC TYPE C (Daylight)

FIG. 30. TYPES OF PANCHROMATIC EMULSION, A, B, AND C. (Courtesy Eastman Kodak Co.) Visible violet begins just before $400\text{ m}\mu$ (40 on the scale), highest visible green is at $550\text{ m}\mu$, and red sensitivity ends at about $650\text{ m}\mu$, although the eye responds up to 700 or beyond.

sin, etc. On the other hand, dicyanin is a good sensitizer for deep red, leaving an insensitive gap in the green; such an emulsion is useful for work with a red or orange contrast filter for photography of designs, wood grain, photography through mist, and so on. Where work is required mostly in the orange region, and deep red sensitivity is not required, Orthochrom T, pinachrome and pinaverdol (Ilford Sensitol Green), can be recommended. Newer dyes, especially for the infrared region, are to be found in dicyanin, above mentioned, kryptocyanin and neocyanin.

The sensitivity of some panchromatic plates as manufactured by the Eastman Kodak Company is seen in Fig. 30; these represent the A, B, and C types of material. It will be seen that all of them exhibit the inherent sensitivity from the ultra-violet up to 500 $m\mu$, but that the ratio this region bears to the region of longer wavelength varies. The upper spectrogram in each case represents the response to incandescent electric light, the lower one to daylight. Incidentally, these pairs give an excellent idea of the difference between daylight and artificial light as regards spectral distribution. It may be noted, too, that the red-sensitivity appears to extend further into the red in the case of incandescent light, but this, of course, is due to the greatly increased energy of the latter in the red region. As explained in the chapter dealing with sensitometry, the spectral character of the light must be taken into strict consideration in making any measurements of either the speed or the color-sensitivity of panchromatic emulsions. Many of the spectrograms published in the early literature are entirely misleading at first sight, because they were made with artificial light, often incandescent gas, and for the same reason any speed measurements of color-sensitive materials can be accurate only if the light sources by which they were obtained are specified. The undyed emulsion is sensitive up to 500 $m\mu$, let us say. We then

add a new band of 500 to 600 $m\mu$ by means of a color-sensitizer to the response. Assuming the useful region in each case to begin in the near ultra-violet at 350 $m\mu$, we have a response in the plain emulsion of 350 to 500 $m\mu$, and of 350 to 600 $m\mu$ in the other; hence the area of response in the spectrum is five-thirds as great in the case of the sensitized emulsion as in the plain one, and its speed will appear proportionately greater if it be exposed in light which is rich in the added wavelengths.

The speed of a color-sensitive emulsion can thus only be estimated fairly by taking into account the spectral quality of the light. The speed numbers given by some manufacturers have in past decades been very misleading, because if correct color rendition of the blue-violet in monochrome is required in the studio, and the necessary filter be used on the lens to obtain it, the effective speed will be reduced again to what it would have been had the speed measurement been made by daylight or properly filtered tungsten light.

We now come to the infrared region of the spectrum, invisible radiation of wavelength extending from about 760 $m\mu$ onwards to 10^6 $m\mu$. The early infrared region has recently become of considerable importance in aerial photography and in much industrial work, both of which are making rapid advance owing to the excellence of the infrared material that has become available. A plain silver bromide emulsion of the boiled type was prepared by Abney, and was claimed to be so red-sensitive that a kettle of boiling water was photographed by its own radiation. The author found that a collodio-bromide emulsion could be sensitized for the early infrared with Benzo Green. Sensitivity up to 800 $m\mu$ has also been obtained by bathing an ordinary plate for ten minutes in a five per cent solution of sodium bisulphite, washing in water for a few minutes, and then bathing again in a one and one-half per cent solution of sodium carbonate. Infrared sensitizing is now obtained by the

116 PHOTOGRAPHIC EMULSION TECHNIQUE

addition of dyes to the emulsion. Dicyanin was used in 1919, being discovered during the researches carried out during the 1914-1918 war to produce sensitizers that had previously been made only in Germany. Kryptocyanin was produced later, sensitizing for the region between 700 and 800 $m\mu$, with a max-

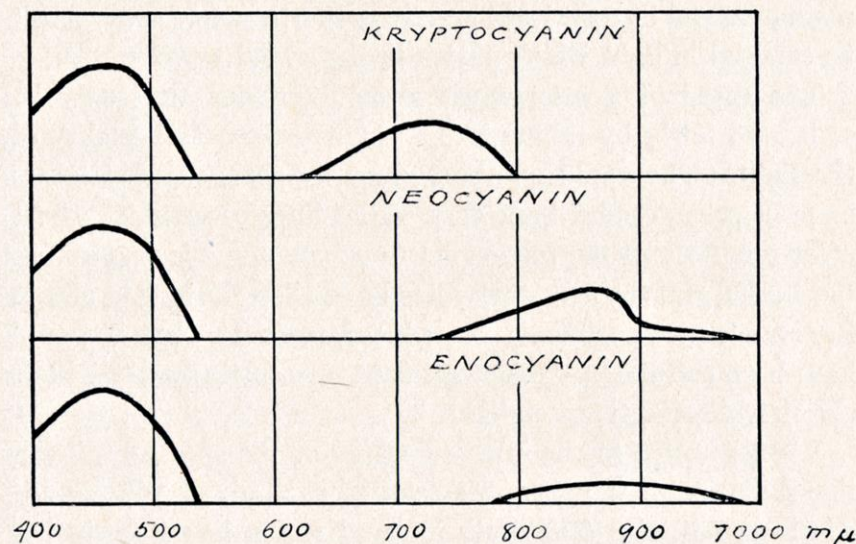


FIG. 31

imum near 750 $m\mu$. It is a particularly interesting dye for experimental work because it can be used with little fear of fog, and will yield plates of good keeping quality. Later, in 1925, neocyanin was discovered, which extended the sensitive region to 950 $m\mu$. One of the carbocyanins, xenocyanin, gives a maximum at 960 $m\mu$ and extends right up to about 1,200 $m\mu$. Certain emulsions sensitized with it have a response up to 1,350 $m\mu$. Some of the responses of infrared sensitive emulsions are seen in Fig. 31. Tetracarbocyanins have been prepared by Dieterle and Reister⁶ which are claimed to sensitize two or three times as highly as the corresponding acetoxy-substituted dyes. A

method of preparing nonacarbocyanins for infrared photography beyond 11,000 $m\mu$ is described by these authors. According to Clark,⁷ plates which are to be used for spectrographic work beyond 900 $m\mu$ must be hypersensitized in order to obtain practically useful speeds. These later infrared sensitizers are not at present commercially supplied, but are prepared by manufacturers for their own use. Dicyanin, kryptocyanin and neocyanin, however, can be obtained.

In Fig. 32 is seen the most recent infrared introduction of the Eastman Kodak Company, which is applied to plates and films



Courtesy Kodak Limited, England

FIG. 32. WEDGE SPECTROGRAM OF INFRARED PLATE AND FILM FOR AERIAL PHOTOGRAPHY

for aero work. It has a wide band of sensitivity, but when this is restricted by the use of an infrared filter, the emulsion is stated to be many times faster than previously existing materials.

FILM PACK EMULSIONS. — Where separate emulsions are used in color-photography for the three primary images, plates may be used in a split-beam or one-shot camera, or films may be laid one over the other in the form of a sandwich and the rays from the lens made to pass through the top film to the one beneath it for the green impression, and thence to a third film which receives the red impression. In such a sandwich, the top film is an un-color-sensitized emulsion, sensitive merely to blue-violet.

For readier separation in a one-shot camera, three distinct emulsions are frequently used. One of these is panchromatic or red-sensitive, one orthochromatic or green-sensitive, and the third normal or "color-blind." When three films are used in

118 PHOTOGRAPHIC EMULSION TECHNIQUE

the form of a tripack, three *similar* emulsions are usually employed. The most obvious order is an upper ordinary or blue-violet sensitive film facing the lens with a green-sensitive film next, screened with a yellow filter which may be incorporated in the top emulsion or coated as a yellow filter layer on the base of the upper film or used as a thin sheet of dyed gelatin between the two films. This yellow filter also suffices to suppress the

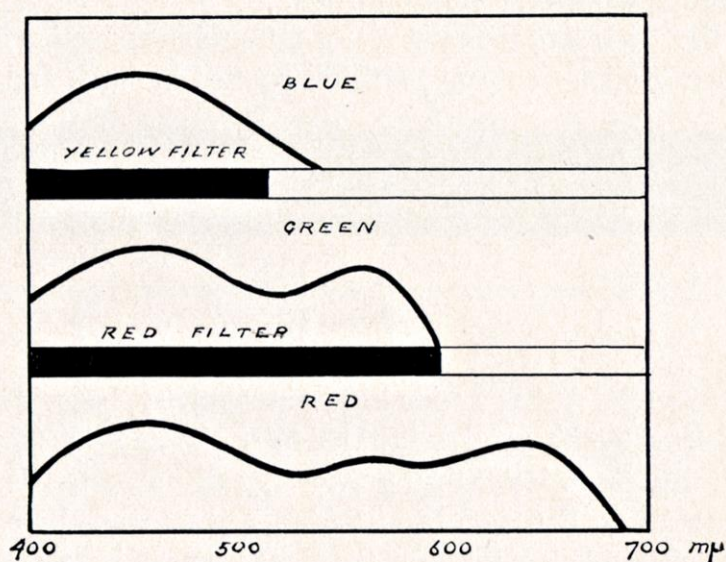


FIG. 33

blue-violet in the back (red response) film if the latter is made red-sensitive only and not fully panchromatic, as, for example, if sensitized with dicyanin. If it be panchromatic, then a red filter must be used. As there is already a yellow one screening the green-sensitive emulsion, the second filter may be magenta, since magenta + yellow = red.

Naphthol yellow or brilliant yellow serves as a good first filter dye; azo rubine, crocein scarlet or rhodamin G will then serve for the red screening component. The general scheme is

seen in Fig. 33. The filtered responses of a commercial tripack (Defender) are shown in Fig. 34. In any attempt to experiment with tripack emulsions, it must be remembered that as the three elements are exposed simultaneously, the relative *filtered* speeds of the three members must be equalized. The

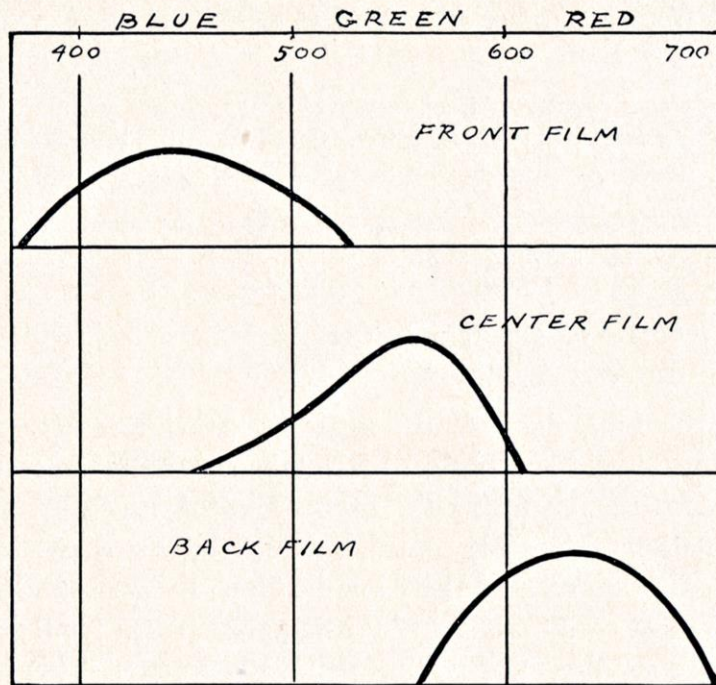


FIG. 34

light is considerably diminished by its passage through the front film, which must therefore have the highest possible transmission, but the lowest sensitivity. The intermediate or green-sensitive film must also be sufficiently transparent to admit of the necessary amount of light reaching the back (red) member. The Defender tripack utilizes more heavily coated emulsions for the blue- and green-sensitive components, so that higher contrasts may be obtained; this is of course the equivalent of allowing a longer time of development for the yellow

printer in three-color work. Alternatively, different types of emulsion may be selected, the aim being that the three images obtained on development are of equal gamma and as far as possible of similar density range.

The following typical specification is made up from data obtained from a number of published patents dealing with tri-packs:

Front emulsion. Coating weight 40–50 mg per dm².
Average grain size 1.2–1.8 μ . Speed 80–120 H and D.
Percentage transmission to yellow light, 35–40%.

Middle emulsion. Coating weight 60–70 mg per dm².
Average grain size 2 μ . Speed 250–300 H and D.
Percentage transmission to red light, 30–35%.

Back film. Coating weight 110–130 mg per dm².
Average grain size 2.5 μ . Speed 1000–1500 H and D.

In assembling the Defender tripack, the two front films, blue- and green-sensitive, are placed face to face, with the base of the blue-sensitive film facing the lens. The third member of the combination is faced lensward, shielded by a red coating on the base of the green-sensitive middle film. Experimental packs can be most easily made up by using glass plates for the front and back members and a film for the middle one. This fact is mentioned on account of the difficulty which may be experienced in coating film base in the laboratory with sufficient accuracy.

The filtering of the blue-violet rays from the green recording film, if not effected by the use of a self-screened emulsion, can be done with a very thin layer of gelatin stained with tartrazin or naphthol yellow between the two emulsions. As tartrazin transmits some ultra-violet, and aesculin or ultra-violet filter should be used on the camera lens. If the red filter takes the form of an actual coating on the back of the green-sensitive middle member, a dye such as Congo red, which is easily decolorized by an acid fixing bath, should be used. Carmine L,

lanafuchsin SB, and tolan red are also mentioned by Wall for this purpose.⁸

The use of a bipack is involved in *two-color* photography. Here the factor of the filter dyes and the speed of the emulsions must again be adjusted so that equal exposure is required in each member for a white object. For two-color work in daylight the Eastman Kodak Company recommends Wratten filters No. 28 and No. 40A, or No. 28 and No. 40 for incandescent tungsten light. Similar color analysis can be obtained by the use of two films as follows:

Front. A fully green-sensitized emulsion, using a Wratten Aero No. 1 or a K-2 filter on the lens.

Back. A panchromatic emulsion.

Interleaf. An orange filter between the two, or an orange coating on the base of the orthochromatic film, both emulsion surfaces facing the lens.

The performance of experimental two-color packs can be properly checked only by tests with the spectrograph (See Chapter XII).

The term monopack is used for a plate or film that comprises a series of non-separable emulsion layers coated one on top of the other, the emulsions being self-screened to effect separation, or dyed material being coated between the sensitive layers. Selective sensitization alone is not adequate. The idea dates back to 1891, when an English patent was granted to H. Kuhn. By straightforward development, the appropriate colors are obtained as silver deposits in each layer. These three black-and-white separation negatives are then converted into the respective color images either by the production of a dyestuff in the parts occupied by the silver, or by *destroying* dyes already incorporated in the emulsion layers, or by dissolving out the negative images and color-developing the remaining (unexposed) silver bromide.

In 1905, K. Schinzel, then a clerk but seventeen years old, coated a plate with three layers of emulsion, each layer being sensitized for one of the three primary colors, but dyed with the color complementary to it. Thus the red-sensitive layer would be dyed cyan, the green-sensitive layer magenta, and the blue-violet-sensitive layer yellow. It was Schinzel's idea, after developing and fixing the exposed monopack, to treat it with a weak solution of hydrogen peroxide. The dyes to be used were such that through the catalyzing action of the reduced silver they would be decolorized to an extent proportional to the different densities. *Color formers* instead of actual dyes were shortly afterwards suggested by this inventor.⁹

The first Mannes and Godowsky patent¹⁰ described an upper self-screened emulsion layer on top of a rapid red-sensitive emulsion. This two-color monopack was developed and fixed in the usual way, the reduced images being afterwards converted into silver ferrocyanide, one for use as a mordant for a basic orange dye; this was done by means of a solution *the diffusion of which could be controlled*. The other (ferrocyanide) image was then toned with a blue-green toning bath. From this brief description, the beginning of the modern monopack can be appreciated.

A three-layer process was meantime worked out by Dr. Bela Gaspar, whose prolific patents date from about 1930. Using black-and-white separation negatives obtained with a split-beam camera, and making from them separation positives, he employed for motion-picture printing in color, nitrate film stock which was coated on one side with a blue-dyed emulsion and on the other side with first a yellow-dyed, and then a magenta-dyed emulsion. The dyes were destroyed on development in proportion to the presence of developed silver; the image was then bleached and the residual silver bromide converted into chloride, on which the sound track was developed. The whole film was then fixed in hypo and all remaining traces of silver

removed, leaving a dye image of great brilliance. Such film was of course applicable to printing only.

In a subsequent process,¹¹ a monopack for exposure in the camera is described. A blue-sensitive layer is coated on the support first, and this receives the lens image. On top of this are coated the green and red layers. A distinguishing feature is that, to speed up the material, dye generators, rather than actual dyestuffs, are used. The blue-violet emulsion, it is suggested, may contain about fourteen grams each of gelatin and silver halide per square meter; the yellow (complementary) dye generator being 0.85 gram per square meter of 1-phenyl-3-methyl-pyrazolone-5. The green emulsion layer is color-sensitized with 2-methyl-1-ethyl-pseudocyanin iodide, and contains a dye developer of one gram per square meter of 1-amino-8-naphthol-3:6-disulphonic acid, which is rendered insoluble through precipitation within the emulsion by triphenylguanidin acetate. This layer is made self-filtering by the addition of 0.75 gram per square meter of tartrazin. The top layer is color-sensitized with pinacyanol, using one gram per square meter of diphenylguanidin acetate, and colored by a suitable red dye. The film is developed, fixed, and washed, and the dyes in the two lower layers generated by treatment with a nearly neutral solution of:

Water	100	cc
Sodium acetate	10	g
Diazosulphanilic acid	0.5	g

This is used at a temperature of between 3° and 8° C.

The film, after being washed and dried, is treated with a blue dye solution, the dye being precipitated in the top layer. The dyes are then destroyed in proportion to the silver deposits of the images by treatment with an acid solution of thiocarbamide.

In the Kodachrome process, after straight development of the three primary images, the reduced silver is dissolved out and

the residual silver bromide is exposed and treated with a blue-green developer. An acid bleach is allowed to diffuse through the two upper layers, the lowest remaining blue-green. In the two upper layers the metallic silver is converted into silver chloride. This is next exposed and developed with a magenta-forming developer. Then follows the next bleach which is confined by controlled diffusion to the top layer only, where once again the dye is destroyed (magenta) and the silver converted into silver chloride. This is exposed and color-developed yellow, after which all that remains is to dissolve out the silver with a solution such as Farmer's reducer (ferricyanide and hypo).

It had been known at the time of the early experiments that many developers produced more or less insoluble dyes by interaction with the silver deposit. Pyrogallol, the oldest known, gives orange, amidol yellowish-red, while blue dye images are given by leuco-indophenols and leuco-indamines and indoxyl. Red images are given by the leuco-azomethines and thio-indoxyl. However, in alkaline (carbonate) solution they are readily re-oxidized by atmospheric oxygen with the production of colored fog. The chemical story of the investigations which led to modern solutions of the problem is well told by Karl and Ludwig Schinzel in their various articles in *Das Lichtbild*.

In any experimental work on monopacks, where dye generators which are either insoluble or not diffusible, are mixed in the emulsion layers, the remaining unused generator must be easily washed out; for example, with caustic alkali. The above authors¹² state that for color photography by simultaneous color development, coupling components which give the appropriate dye in each layer with the oxidation products of a suitable developing agent or by simultaneous oxidation by the silver halide, must be mixed in the three layers.

The insoluble salts of the naphthols or their derivatives and

analogues, the arylsulphonamides, pyrazalones and acidic methylene compounds can be added to the layers. Calcium or barium hydroxide, guanidin or sodium glycolate may be added to maintain stability. The carboxyl or sulphonic acids of couplers may be added to the layers in the form of insoluble or barely diffusible salts with inorganic or preferably colloidal organic bases. The coupling component is used in quantity equal to about one-half of that of the silver halide present. A developer containing one per cent of p-amino-dimethylanilin hydrochloride and five per cent of sodium carbonate is recommended.

One of the difficulties in tripack manufacture is the thinness of the emulsion layers, which is indispensable in order to avoid scatter. Present day precision coating machines are capable of coating layers which when dry are as low in thickness as 3 to 4 μ . Optical contact, *i.e.*, the actual coating of each layer on top of the other, is necessary and the three coatings of a monopack must provide definition which it is impossible to obtain with any form of tripack in which three separate films, however thin, are employed.

The chemistry of direct and indirect dye couplers and of color formers has already given rise to a literature of its own, and it is impossible to do more than touch on some of the aspects of the monopack and its problems, in these pages. Recourse to the patent literature is necessary to any form of study, though an immense amount of information will be found in the articles of the Schinzel brothers already mentioned.

For the purposes of experiment, when two (or three) layers of emulsion have to be processed, an addition of alcohol and glycerin to the bleaching solution will help to prevent penetration to the lower layers. The actual emulsion used can be made to assist in this direction also; thus the lower emulsion, first coated, may be made with a gelatin having a low water absorp-

tion coefficient, which is in turn hardened to the maximum extent, while the upper emulsion is made with a soft gelatin which swells readily and to which a small proportion of sorbitol is added. It should be pointed out, however, that only comparatively crude experiments can be envisaged with monopacks without refined facilities for both coating and processing.

Although it is beyond the scope of this book to enter into the manufacture of emulsions containing color formers, the following formulas for producing colored images by direct development of silver bromide emulsions may be given. A basic developer is used as follows:

Sodium carbonate	40	g
Sodium sulphite	20	g
2-amino-5-diethyl aminotoluene hydrochloride	0.5	g
2 per cent potassium bromide	30	cc
Water	1000	cc

The blue-green coupler is:

2-4-dichloro-1-naphthol	1	g
Acetone	5	cc
Basic developer	250	cc

The magenta coupler is:

p-nitrophenylacetonitrile	0.05	g
Acetone	5	cc
Basic developer	250	cc

The yellow coupler is:

Aceto acetanilide	0.5	g
Acetone	5	cc
Basic developer	250	cc

The image is formed in color on development with the above solutions, and is afterwards fixed in plain hypo solution. The reduced silver is then removed by treatment with hypo-

ferricyanide when the clear dye images are left. In triple-coated film it is conceivable that the dye couplers could be incorporated in the respective emulsions, the one basic developer then producing simultaneously the three colored images. In the formation of such a monopack it would facilitate production if a very thin layer of 3 to 4 μ of gelatin were coated between each emulsion layer as is done in the case of Kodachrome film.

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