

PART 2: Chapters VII - XIV

PHOTOGRAPHIC EMULSION TECHNIQUE

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1941
AMERICAN PHOTOGRAPHIC PUBLISHING CO.
BOSTON

PHOTOGRAPHIC EMULSION TECHNIQUE

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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

CHAPTER VII

X-RAY AND ULTRAVIOLET

X-ray Emulsions — Intensifying Screens — Lippmann Emulsions — Ultraviolet Plates.

IN the first few years following Roentgen's discovery of the X-rays, it was found by empirical experiment that plates coated with a slow silver bromide emulsion containing the least possible quantity of silver iodide, gave the fastest response. High speed to visible light had very little to do with the matter. It must be remembered that at this time X-rays were produced with very crude tubes, excited by Ruhmkorff coils fitted with the old hammer type of interrupter, capable of giving a spark in air of only a few inches. Exposures of as much as thirty *minutes* were quite common for thick parts of the body, and it was not at first understood that short-wave radiation had a greater penetrative power, without which the longer waves could not produce a result, no matter what *quantity* of energy was used. Fig. 35 shows how the penetrative power increases with decrease in wavelength in the case of aluminum.¹

While the action of X-rays on photographic emulsion films is very similar to that of visible light, examination of microscopic sections through the developed film shows that the rays produce an equal distribution of grains of reduced silver throughout its whole thickness. It is thus evident that greater density can be obtained by increasing the thickness of the layer of sensitive silver salts, or alternatively its silver halide content. As stated, however, X-rays of different frequencies do not have an equal quantitative effect, and while the shorter wavelengths

are needed for penetration of deep or thick parts of the body or for metallographic work, the shorter or "soft" rays produce the greatest blackening. For study of the sensitometry of X-ray photography the reader is referred to the work of Wilsey and Pritchard.²

In medical practice, the peak voltage used, which is a direct measure of the penetrative power, varies between 35 and 90

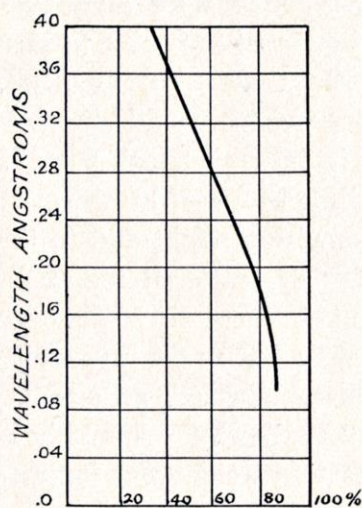


FIG. 35

kilovolts. This is ordinarily obtained from a transformer, and after rectification is applied to the tube. The modern X-ray tube has a cathode which is heated by a local circuit, and as the heat is increased, so the electrons emitted by it lower the resistance of the path between it and the *anode*, and so control the hardness of the radiation generated at the anode surface. Over this range the one type of X-ray emulsion functions so satisfactorily that different emulsions have never been made for work in different parts of the X-ray spectrum.

According to Charlesby,³ the response of a photographic emulsion to incident X-radiation is appreciably affected by the

absorption of the beam within the film layer, a fact that must be taken into consideration in X-ray sensitometry. This point is mentioned, inasmuch as X-ray plates are used to some extent in the measurement of radiation, which is determined by their photographic blackening powers under controlled development.

During the first years of X-ray photography, numerous substitutes for silver *bromide* were investigated, the trend of thought being that heavy salts of silver (such as silver tungstate, for example), or perhaps salts of heavy metals themselves, having a high molecular weight, would absorb more of the radiation and convert it into chemical energy. An alternative thought was that the addition of heavy, inert metallic salts incorporated in the emulsion might add to the effect of the exposure by secondary or scattered radiation. The results of countless experiments in these directions ended in a verdict for straight silver bromide; but as the rays were only partially absorbed by their passage through an ordinary emulsion layer, it became obvious that the plates should be coated as richly as possible. Hence coating weight was increased from, say, 120 milligrams per square decimeter to 180 or more milligrams, in some cases by giving a double coating. Too thick a film has, however, many disadvantages.

Plates of excellent service were produced along these lines, reducing exposure to a fraction of what had previously been necessary, and at the same time immense advance was made in the construction of apparatus for producing the high tension supply and in the tubes themselves. A very important advance was next made by the introduction of so-called intensifying screens. A piece of card or celluloid coated with a layer of artificial Scheelite (calcium tungstate), glows a brilliant blue to bluish-white under the influence of X-rays, and the fluorescence excited provided photo-actinic light about five times as

effective on a silver bromide emulsion as the original rays. Hence by placing the active surface of such a screen in close contact with the emulsion film during exposure, the latter was so greatly reduced that the great bulk of radiographic work quickly came to be done with intensifying screens. In so doing, the problem of the emulsion maker was somewhat changed in complexion, for now emulsions were needed which were sufficiently sensitive to X-rays themselves, but had also an optimum response to the blue rays fluoresced by calcium tungstate.

The fact that only a low proportion of the incident rays is absorbed by both intensifying screen *and* emulsion, led to the idea of coating film base with emulsion on both sides, when two intensifying screens could be used, one on either side of the double-coated film. An English patent was applied for by the author in 1916 for the use of two intensifying screens in this manner with thin glass plates (X-ray film had barely made its appearance at this time), but the diffusion of the image on the far side owing to its separation by the glass, led to its abandonment. Later, a double-coated film of magnificent quality, made by the Eastman Kodak Company, overcame this problem of definition, and double-screen technique became standard practice, except where the finest possible definition was required, or for "thin" subjects such as hands, wrists, etc. The grain of the calcium tungstate crystals not only tends to give a slight granularity to the image, but each tiny crystal acts as a source of secondary radiation which throws off rays of the same wavelength as the original beam in all directions, and so causes diffusion. The general use of intensifying screens naturally led to some attempts to modify the emulsions, as at least eighty per cent of the exposure reaction is probably that obtained from *visible* (fluorescent) light. At one time plates were even specially manufactured having a maximum response to that part of the spectrum and having a normal coating weight. Present-

day emulsions, however, are composed chiefly of silver bromide and can be used equally well with or without screens.

Yet another change is now affecting the position. Inasmuch as a full exposure for a deep part of the body involves gross overexposure of the soft tissues, detail in the latter is necessarily lost. To overcome this drawback, a plain X-ray film is being used in many cases on top of the sandwich of intensifying screen — double-coated film — lower intensifying screen, so that it receives relatively only about one-tenth of the effective exposure of the double-coated film. The un-intensified film thus gives the detail in the soft parts, while the screened film is correctly exposed for the main subject. A method was patented by Dr. Leonard Levy and the author⁴ for incorporating the calcium tungstate in cellulose acetate base when casting the latter, so that the film would be automatically self-screening.

A general emulsion for X-ray work, providing the necessary density and gradation, and suitable for use with or without screens, may be made as follows:

A. Water	3000 cc
Nelson's X-opaque gelatin	360 g
Ammonium bromide	520 g
Potassium iodide	6 g
B. Silver nitrate	600 g
Water	150 cc
Stronger ammonia water	to redissolve
C. Silver nitrate	200 g
Water	800 cc
10 per cent nitric acid	10 cc

Weigh out the salts and gelatin in *A* and allow them to stand in the water for four hours. Raise to 110° F. (43.3° C.) and cool back to 90° F. (32° C.). Add *B* rapidly from a jug at room temperature with gentle stirring. After an interval of three minutes, add *C* at 120° F. (49° C.) through a four milli-

meter nozzle, with rapid stirring. Then immediately add 800 grams of American Agricultural Co.'s high viscosity gelatin, and stir until dissolved. The crock is stirred while pouring in the gelatin powder. Take to 105° F. (40.5° C.). Then set quickly in cold small crocks in ice water. Wash after twenty-four hours until free from ammonia, then digest from one to two hours at 120° F. (49° C.).

Final additions are:

2 per cent solution of phenol in spirit	600 cc
5 per cent chrome alum solution	50 cc
10 per cent potassium bromide solution	100 cc

Total bulk is 12,000 cc. Recommended coating weight, 200 to 220 milligrams per square decigram.

A practical reason for keeping the iodide low is that in fixing tanks such as are generally used, a high percentage of silver iodide will accumulate in the hypo solution and will convert part of the silver bromide in films subsequently immersed into silver iodide, which takes very much longer than silver bromide to fix.

Before leaving the subject of X-ray emulsions, it should be stated that investigations in recent years have indicated that fluorescent screens glowing a color other than that of calcium tungstate, for example green or orange, might be usefully employed in conjunction with a highly color-sensitized film. A zinc sulphide screen, for example, fluoresces bright green or bluish-green according to the method of manufacture, and with an orthochromatic emulsion will admit of excessively short exposures. Levy and West⁵ have done much work in this direction, and have evolved a special screen for this technique. Whereas the fluorescence spectrum of calcium tungstate extends roughly from 370 to 470 m μ , that of their "fluorazure" screen is compressed into a sharply defined spectral band extending from 390 to 490 m μ .

ULTRAVIOLET SENSITIVE EMULSIONS. — While silver grains are sensitive to light of practically all wavelengths shorter than the visible violet, the ordinary emulsion shows a distinct slackening off in response at 280 $m\mu$. This is primarily due to the natural opacity of gelatin to the ultraviolet. The response of the emulsion decreases steadily as wavelength decreases, showing a marked drop at 240 $m\mu$, and ending altogether at about 200 $m\mu$. Some attempts have been made to sensitize emulsions to ultraviolet by the addition of a sufficiently concentrated solution of sodium salicylate (Tien-Kin). Application is also made to the surface of the emulsion of oil or vaseline, which absorbs ultraviolet energy and converts part of it into fluorescent light of longer and more photographically active wavelengths. Diminution of the gelatin vehicle, with a consequent exposure of the silver bromide filtered with a minimum of colloid, still remains the best practice, as originally suggested by Schumann,⁶ whose name is usually associated with this type of plate.

Schumann's technique is as follows: a plain silver emulsion is prepared, rather weak in gelatin. A five per cent concentration of gelatin is suitable. The quality of the gelatin is stated to play an important part, and Nelson's No. 1 is particularly recommended. The emulsion is ripened and digested at one operation by heating to 140° F. (60° C.) for a sufficient time, and is then set in ice water and washed. Very pure ingredients should be selected and, as a small trace of organic matter appears to be prejudicial, freshly distilled water should be used throughout. By keeping the washing water cold (42° to 45° F.), swelling of the gelatin will be minimized. The washed emulsion is next diluted with a large volume of hot distilled water, breaking it down to a fraction of the usual concentration, and this very dilute emulsion is poured into a scrupulously clean tank on the bottom of which has been placed the glass plate that is to be coated.

The temperature should not be above 65° F. for this sedimentation operation, otherwise there will be a tendency towards halation. The silver bromide, with just enough associated gelatin to make it adhere to the glass in a good continuous film, deposits gradually, and when the coating is sufficient the supernatant liquor is very carefully drained off and the plate allowed to dry in a flat position. Using a fluorite prism, and plates prepared in the above-indicated manner, the whole apparatus being in vacuo, Schumann is stated to have photographed the spectrum of hydrogen to 120 m μ .⁷

The individual worker will find by experience the best procedure with his own working conditions and apparatus. Plates so prepared are insensitive to light of longer wavelength than about 300 m μ . While Schumann worked largely with a pyrogallol-soda developer, Lyman⁸ recommends an ortopotash formula. Any free bromide in the developer appears to increase the grain size of the image, and for that reason should be avoided.

An alternative method of treating plates coated with a slow or medium speed emulsion such as an X-ray type has been given by Duclaux and Janet.⁹ The plates are placed horizontally in a dish or tank filled with ten per cent (by volume) of concentrated sulphuric acid in water, and are kept for four hours at about 77° F. They are then carefully removed and washed in a very gentle current of water, and then dried. The treatment has the effect of removing both gelatin and silver, except for a very thin layer. This is stated to give plates two hundred times faster than commercial Schumann plates.

LIPPMANN TYPE EMULSIONS. — This type of emulsion yields a color-sensitive, fine-grained plate suitable for experiments with the well-known Lippmann process of natural-color photography. The process depends on the interference of light waves traversing the emulsion before and after reflection from the

back of the plate, which is in contact with a mercury mirror. It thus necessitates an exceedingly fine grain; Lippmann emulsions are usually referred to, in fact, as *grainless*. A method described by Lehmann is as follows:

A solution of gelatin is first prepared:

A. Hard gelatin	20 g
Water	390 cc

This is dissolved and filtered through spun glass (glass wool) or cotton batting (wadding) and used at 95° F. (35° C.).

To 80 cc of the *A* solution add

Distilled water	10 cc
Silver nitrate	4 g

To the balance of solution *A*, add and dissolve 3.2 g of potassium bromide. Taking care that there is no froth on this, it is slowly poured into the gelatin-silver solution at the same temperature, stirring fairly gently during the precipitation and for three and one-half minutes afterwards.

The following sensitizing dyes are then added immediately:

Pinacyanol (1:1000 alcoholic solution)	4 cc
Orthochrom T (1:1000 alcoholic solution)	4 cc
Acridin Orange (1:500 alcoholic solution)	4 cc

This mixture of dyes must have been previously warmed to 86° F. (30° C.). It is added slowly with gentle stirring, not more than forty-five seconds being taken. Under no circumstances must the emulsion be subjected to any further heating, the object being to avoid grain growth and fog formation.

A very thin coating is applied to glass which has been so perfectly cleaned that, if breathed upon, the condensation is even all over and clears quickly. The coated plates are laid on a cold slab to set, and are then washed in a trough with gently running water. Ten minutes should suffice to remove the potas-

sium nitrate. The washed plates are best dried in a horizontal position; this is stated to give the most brilliant colors.

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CHAPTER VIII

COATING EMULSIONS ON GLASS

Preparation and Cleaning of the Glass—Substratums—Drying Cupboards and Drying Problems—Coating Heads—Ventilation and Heating

THE coating of negative and positive emulsions on glass, at one time the only support available, suffered a severe setback when rollfilm, and later cut film, came into such general use. Plate coating has nevertheless been continuously maintained on a large scale, particularly for the South American markets, and in recent years certain advantages over film base possessed by glass, especially in the photo-mechanical industries, have brought about a decided return to the dry plate. The study of silver halide emulsions necessarily involves coating and testing them upon a suitable base, and for laboratory and investigation work glass is definitely, except where matters specifically relating to film technique are involved, the most satisfactory medium, especially as it lends itself so well to hand coating.

Carefully filtered emulsion of suitable viscosity is coated upon sheets of chemically cleaned glass. A known quantity is poured on and distributed evenly over the surface while warm, any excess over the desired amount having been previously poured *off*. The coated glass is laid on a cold levelling table, where the emulsion sets to a firm jelly within thirty to sixty seconds. The set plates are placed in a dust-free dark cupboard to dry, where they may remain for from four to twelve hours, according to the temperature and humidity of the cupboard and efficiency of the ventilation.

In commercial practice, the glass sheets are washed by a machine in which they are made to pass between reciprocating

brushes and rollers. A cleansing solution such as soda is sprayed on them during their passage through the first part of the machine. They next pass through water sprays, then between rubber rollers which squeeze off the superficial water, and are finally sprayed with a weak solution of chrome alum or sodium silicate, which leaves the surface with a *substratum* or "tooth" which serves to anchor the emulsion to the glass surface and to prevent the danger of frilling or blistering during the processing of the plates.

The chief commercial sizes of plates in use in the United States are 4 by 5, 5 by 7, 8 by 10, 11 by 14 and 14 by 17 inches. Larger sizes are used in photo-engraving work and commercial photography. Four by five plates are coated as 8 by 10 and cut, when dry, into quarters; 5 by 7 would be coated as 7 by 10 and cut into two. The most popular English sizes are $3\frac{1}{2}$ by $2\frac{1}{2}$ (the higher figure is quoted first), $4\frac{1}{4}$ by $3\frac{1}{4}$ (quarter-plates), $6\frac{1}{2}$ by $4\frac{3}{4}$ (half-plates), $8\frac{1}{2}$ by $6\frac{1}{2}$ (whole-plates), 10 by 8, 12 by 10 and 15 by 12 inches. The gauge of the glass increases with the larger sizes; the sheets themselves run about one-sixteenth inch short of the nominal size in either direction to insure easy fitting in plateholders.

The sheets of glass are delivered in crates, and require a certain amount of sorting. The glass must be fairly flat, uniform in thickness, and as colorless as possible. It must also be free from bubbles and flaws. Drawn glass, which has come into use recently, may have slight channelings, the worst of which must be rejected, but "flat" negative glass is ordinarily slightly curved, and the concave side is placed uppermost on the coating machine. The plates, after washing and drying, must be inspected to make sure they are all concave side to one direction so that no delay is caused in feeding them to the machine.

It is never advisable to use old negative glass from which the

developed film has been removed. The original image is liable to appear as a "ghost" in the newly exposed picture, and is probably the explanation of the only genuine "spirit" photographs which have puzzled laymen. Clerc states¹ that it may be supposed that the presence of ultra-microscopic particles, probably of metallic silver in solid solution in the glass, are the cause. Suitable glass in small quantities, known as negative glass, can be obtained for experimental purposes from suppliers of photo-engraving materials, such as Geo. Murphy, Inc., of New York, etc., or of course from any firm of glass merchants.

A solution of potassium dichromate of two ounces to the pint, to which two ounces of sulphuric acid has been very cautiously added slowly, with stirring, is very useful for cleaning small quantities of glass for experimental work. It may be applied with an old, flat nailbrush, but rubber gloves should be worn and care taken not to get any splashes on the face or skin, as the chromic acid is very corrosive. The glasses must be very thoroughly washed under the tap afterwards and put into a clean plate-rack to dry; this rack should be kept entirely for this purpose. Another method is to brush them with a hot two per cent solution of caustic soda, afterwards washing thoroughly under the tap. Substratuming is done by dipping them into a dish containing a two per cent solution of chrome alum after the final rinse and racking them *without* further rinsing. They should be dried in a perfectly dust-free cupboard.

As a great deal of the success with test emulsions depends on the efficacy of the drying cupboard, this should next be described. Dust and bacteria are arch enemies of the plate maker. Mold spores are invariably carried on dust particles. A speck of dust dropped on to the gelatin-coated glass may deposit a spore which finds an ideal medium for growth, especially if the plates are dried slowly in a somewhat humid warm atmosphere. The gelatin itself, in the process of manufacture, may

pick up bacteria which remain latent and will ultimately infect the emulsion. Certain types of bacteria develop below the surface (anaerobic types), and cause the formation of tiny liquefied local spots. Micro-organisms in some cases produce alkaline growths, in other cases they are acid. The acid growths will desensitize the emulsion and usually produce white spots in a negative. The alkaline growths tend to produce black

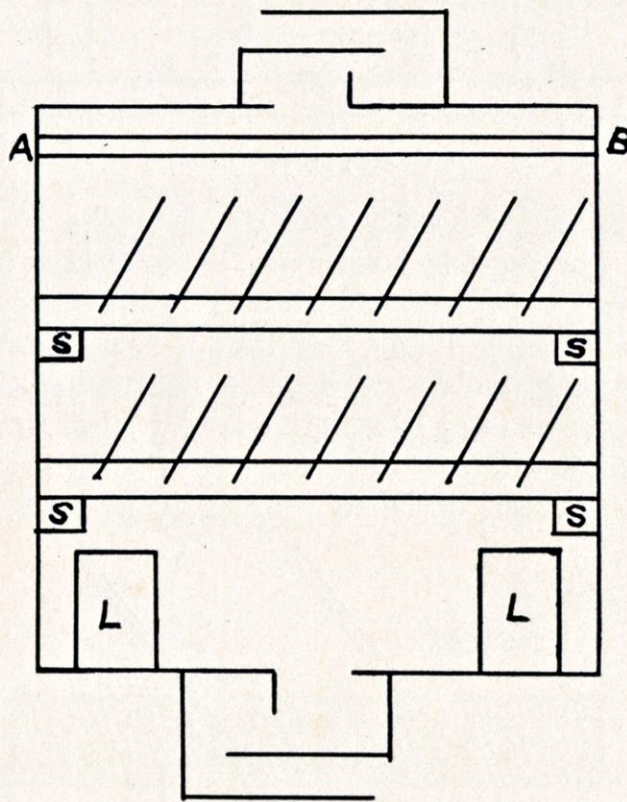


FIG. 36

spots. There is plenty of dust in addition which carries no bacterial infection, but which, if it settles on the film while the plates are drying, may produce spots of one kind or another, or alternatively may cause scratching of the emulsion if the

plates are packed film to film. The usual procedure, of course, is to pack plates with thin card edge-separators between each pair of plates.

A diagram of an easily constructed small cupboard is shown in Fig. 36. If made 36 inches wide inside, 36 inches high, and

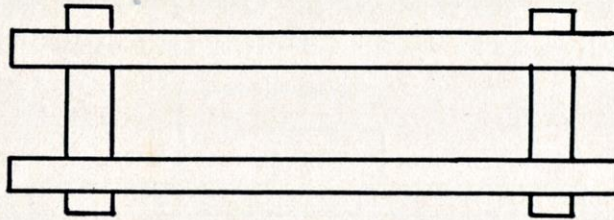


FIG. 37

12 to 14 inches deep it will accommodate a couple of dozen plates or more, 5 by 7 or 8 by 10 inch size, in two racks as indicated. The racks are made movable, resting on the supports *SS* as shown in the figure. If experimenting with papers, several strips of coated paper can be suspended from the crossbar *AB*. Each rack will require two 1 by 1½-inch wood bars, their length being just under the width of the cupboard, attached to two cross pieces as indicated in Fig. 37, so that the complete rack can

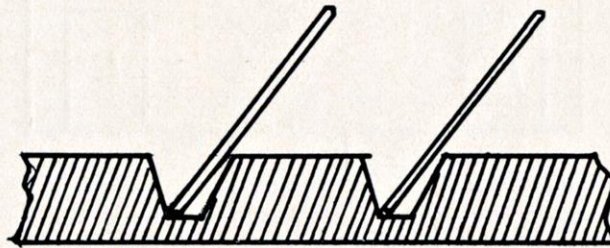


FIG. 38

be laid on the supports. The rack bars must be notched at equal intervals as shown in Fig. 38, to support the plates more or less vertically. Ventilation, top and bottom, must be fully light-trapped. An entry at bottom and exit at top can be built up

with baffles in any simple way with a little ingenuity. Two 15-watt Mazda lamps, *LL*, completely concealed by inverted cans with baffled ventilation holes, will provide ample heat for a cupboard of this size, the hot air rising and causing some circulation. The temperature should not rise above 90° F. The cupboard can equally well be mounted on the wall an inch or two above a radiator, the inside lamps being then unnecessary, or a concealed heater such as an electric flatiron, used in series with a resistance to reduce the heat, may be adopted. The heat in any case should not be switched on until the plates have been in the cupboard for at least half an hour. A door is not shown in the figure, but it is best made practically the entire size of the cupboard. It must of course be made thoroughly light-tight, and the whole of the inside should be painted with dead-black varnish.

The coating of the glasses requires to be perfectly even, of a carefully controlled thickness, and free from spots, bubbles, or blemishes. Emulsion is not, as a rule, used the day it is prepared, but is set off after making up and filtering, and remelted for coating next day, with practically no stirring. Before the coating, it is warmed to 105° – 110° F. and stood for

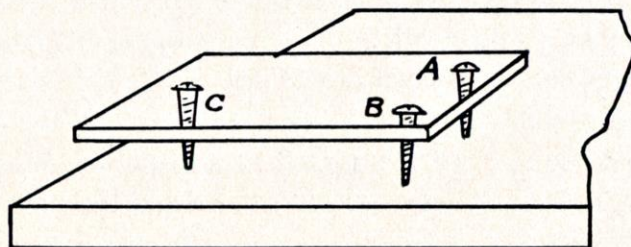


FIG. 39

from fifteen to thirty minutes. A convenient levelling table can be made with a sheet of plate glass three-eighths or one-half inch thick, resting on three two-inch nickel screws (Fig. 39).

The screws are set only about half an inch into the bench or table, leaving an inch and a half above it. Care must be taken that if two such screws are in line, the third must be placed symmetrically at right angles to this line, so that the three screw tops form the corners of an equilateral or isosceles triangle.

The plate glass is laid on top of the three screws and levelled. Setting a spirit level along a line between the two screws *AB*, these are adjusted until that side of the glass is dead level. The spirit level is then laid at right angles, that is, along the line from *C* to *AB*, and screw *C* is adjusted. Butterfly flanges may very usefully be soldered on to the under part of screws so that they can be turned without having to lift the glass plate every time. A piece of 12 by 16-inch glass is a useful size, taking four 5 by 7 or half a dozen 4 by 5 plates comfortably at one time. The plate glass should be kept in a dish of cold water at about 40° F. until just before coating, and the plates laid on it wet, without wiping the surface. For the sake of uniform work it is recommended that the plate glass be cooled to about the same temperature on every occasion. The glasses themselves should be on the warm side, about 70° to 75° F. to assist even flow of the emulsion. Elaborate setting devices made of metal with plate-glass tops, into which ice-cold water or warm water can be run at will, are used by some, but the simple method just described leaves little to be desired from the point of view of results.

Keeping the size 5 by 7 inches as a good working unit for test work, the volume of emulsion needed per plate is about ten cubic centimeters. Transparency or lantern plates are best coated with six to eight cubic centimeters, but if this is found difficult to distribute evenly, the emulsion may be diluted for coating proportionally. A simple trick of getting the exact coating weight is to use two little beakers as shown in Fig. 40. One, *A*, is clearly marked with a black stripe at a measured

content of, say, 20 cc. The other, *B*, is similarly marked at a content of 10 cc. Beaker *A* is filled with emulsion at about 100° F. to the mark; to avoid bubbles, a piece of washed out cheesecloth or coarse muslin is laid over the top when pouring in. The whole lot, in this case 20 cc, is poured quickly on to

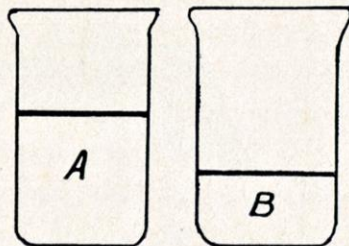


FIG. 40

the middle of the glass plate, which is balanced on the tips of the thumb and fingers of one hand. Quickly, but gently, the glass is tilted so that the emulsion runs to one corner furthest from the coater. It is then tilted in the other direction until it runs to the opposite far corner. By further tilting, it is made to run to the opposite *near* corner, then over to the other near corner. It is given a deft twirling movement to even out the emulsion, and then sufficient emulsion is poured off the glass into beaker *B* to fill it up to the 10 cc mark. The volume of the emulsion left on the plate is obviously the difference between 20 and 10 cc, or the amount required for the area in question. If the glass is not cold, and the emulsion is of the right temperature and viscosity, it will remain perfectly fluid during this operation and will level out nicely. The coated plate is then immediately taken by the other hand at one edge — thumb at the edge and fingers below the glass — and laid on the cold levelling table, and left there until set.

A little practice will make coating come quite easily, and it will be found that plates up to 12 by 15 inches can be coated

quite evenly in this way. But while it is somewhat extravagant, it is strongly recommended that preliminary coating experiments be made with emulsion in white light until the knack has been acquired. The concave side of the glass is coated, and this can be seen by looking along the edge of the glass when held in a vertical position on a level with the eye.

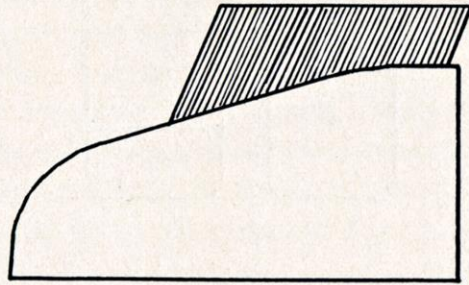


FIG. 41

Setting depends, of course, upon the quality of gelatin used, its concentration, the amount of heat which has been applied, and the finals present in the way of spirit, chrome alum, alcohol and so on. Certain proprietary chemicals are sold to reduce surface tension, and these affect coating to some extent. It should be contrived, from a purely mechanical point of view, that thirty seconds suffices to set the emulsion so that it can be lifted from the levelling table and transferred to the drying cupboard. Evenness of coating can be detected instantly by looking through the coated plate at a low candle-power, clear Mazda bulb. This should not be done with every plate, as it may cause fog. Hand coating of panchromatic plates requires some practice on account of the very low light in which it has to be done, and the curious fact that perspective seems lost in the dim green light of the panchromatic safelight. It is fortunate, however, that panchromatic emulsions are far less sensitive when wet and that, provided *direct* rays are avoided, a

comfortable amount of light is permissible. If the tests on processing show fog, coating light should always be suspected before chemical trouble.

In commercial coating, the glass, having been washed, dried, and stacked in a convenient wooden box (Fig. 41), with the concave sides all one way, is placed on a table near the coating machine, and slightly warmed to a temperature of about 75° F. The sheets are fed on to the machine, the operator wearing white cotton gloves. The principle of the coating machine is indicated in Fig. 42, where the glasses are fed on to a "band" of small diameter rollers, almost touching, which are seen revolving in a clockwise direction. As the plate is laid on the rollers, it is carried forward until it passes under the coating head or spreader, indicated by *S*. It emerges coated with emulsion and passes on to an endless band of felt or blanket running over

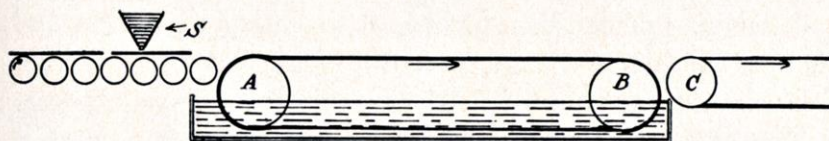


FIG. 42

rollers *AB*, the lower half of the band passing through a tank of cold water to keep it at a sufficiently low temperature to insure setting by the time the coated plate has traveled to the end of the run. The set plates then pass on to a contiguous endless band running over rollers *C*, which are driven at a slightly faster speed. This causes the plates to become separated by intervals of about half an inch, so that they can be easily picked up by the taker-off at the extreme end of the run. The plates are racked, and as each rack is filled it is carried away by another operator and placed in a section of the drying cupboard.

Many variations of this general scheme are naturally possible. In place of the endless band of felt, for example, two parallel metal chains running over a slate or plate-glass bed are frequently used. Chilled water runs along the bed, and the plates actually ride along on the chains with a film of water in contact with the under side. In all cases, it is usual to make a tunnel of the part of the machine where the coated plates are setting, with a light wooden or metal cover, in order to make the travel dust-proof.

A matter that should not be passed over in connection with commercial production, is that certain individuals appear to have a bad effect on the emulsions, and it has not infrequently happened that a man who may be a good coater cannot be employed in this part of the factory. In spite of wearing cotton gloves and although modern hygiene and ventilation, etc., would appear to make such a contingency ridiculous, personal contact and handling of emulsions makes it necessary to suspect and check up personnel when trouble from fog arises after all other likely causes have been properly investigated.

The greatest variation in coating machinery for plates is probably to be found in the character of the spreader. The simplest possible form is that of a V-shaped trough made up of two pieces of flat glass, ground dead true at the bottom; these are inclined to each other at an angle of about 40° by means of two wedge-shaped pieces of wood which also form the ends. As indicated in Fig. 43, the bottom edges of the glasses do not quite meet, but leave a parallel-sided slot of about a sixteenth of an inch, easily adjustable in putting the trough together, through which the emulsion passes to the glass plates as they travel beneath it. The four pieces — the two triangular ends and the glasses — can be taken apart and cleaned after each coating, and then reassembled by means of suitable clips to re-form the spreader. The complete V-trough is supported by uprights at

the sides of the machine, the height above the travel being adjusted to the thickness of emulsion film required. The emulsion is introduced into the trough from a tap leading from a jar standing above the machine, and is maintained at a constant level *in* the trough. In spite of the great simplicity of the V-spreader, in skilled hands it remains one of the most satisfactory coating appliances in practice.

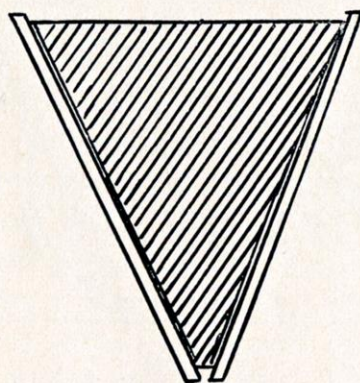


FIG. 43

A more elaborate spreading device was invented by James Cadett, which consisted of a number of tiny silver pumps placed in line, which delivered the emulsion from a number of points to the spreader proper, the length of throw of the pump pistons regulating the volume of emulsion delivered. By controlling this throw, and the rate of the endless band carrying the glass, a very exact quantity of emulsion could be delivered. The emulsion was run out from the pumps on to a silver plate of slightly less width than that of the glass to be coated, and in front of it was a silver roller suspended on cords which almost touched the surface of the plates and distributed the emulsion evenly over the whole width.

The cascade spreader is another type. Here the emulsion is delivered from a tap or set of pumps into a small trough

formed by a strip of silver, *AB* (Fig. 44), attached to a small tube of silver, *T*. When the emulsion has filled the trough to the height of the top of the tube, it flows over and falls down

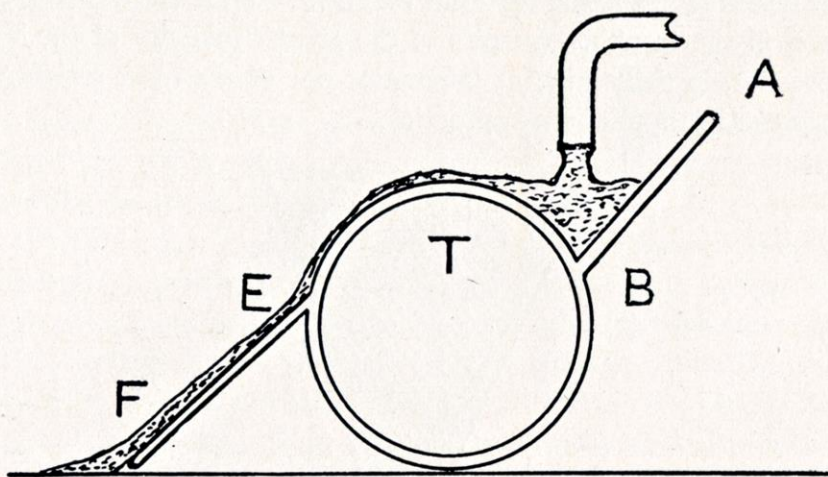


FIG. 44

the cascade, *EF*, which is another strip of silver sheet, the lower end, *F*, of which comes below the tube, *T*, and under which the plates pass in the direction indicated by the arrow. Sometimes a thin strip or "apron" of linen or paper is attached to the bottom of the cascade to provide a more flexible "lead on" to the glass surface. Here again some convenient type of constant level apparatus may be used to control the amount of emulsion falling into the spreader, or it may be controlled by a series of Cadett pumps.

As an example of a commercial plate-coating machine² the following details may be quoted:

Feeding-on belt	4 ft., 6 in.
Adjustable "fence" for guiding the glass in center of this belt	1 ft., 9 in.
Endless belt under emulsion spreader, kept warm by warm water in which the lower part of the belt travels	3 ft., 3 in.
Washing rollers to clean under-side of the coated plates	1 ft., 0 in.

First endless belt for levelling out of emulsion, with separate under tank of cold water	5 ft., 0 in.
First setting belt	7 ft., 0 in.
Second setting belt	7 ft., 0 in.
These two are kept cool by water from one long tank below.	
Dry blanket belt	5 ft., 0 in.

The total overall length of the machine is thus about 34 feet. The setting belts may be of cord, ribbon or flat gauze. Over them is a nineteen-foot cooling tunnel provided with cold coils which cause cool air to fall on the surface of the plates.

A number of points must be taken care of in any form of plate coating. It is hardly necessary to say that uneven distribution is a grave fault, as is any form of streak or friction line running along the length of the plates. Perfect mechanical work and adjustment is needed, and complete freedom from vibration. A direct drive from a worm gear is almost sure to give trouble, and while a high speed motor may be geared down suitably by a worm drive, the drive to the machine should be by belt. The proper control of viscosity, temperature and running rate will have to be found by experiment for any machine, but the emulsion chemist should try to leave the coater as little adjustment to make as possible. Thus all fast negative emulsions should be capable of being coated at about the same speed, while medium slow negative and slow photo-mechanical or diapositive types would form two other groups. The thickness of the glass being usually less in plates which are to be cut to small sizes, some adjustment will be necessary in the height of the spreader or the throw of the pumps, etc., so that here again a whole day's coating of one particular brand or group of sizes is indicated for smooth running.

The modern dry plate must be so perfect to stand up to commercial requirements, that the greatest care is essential in the treatment of the air of the coating and drying rooms. Many

firms — such as Carrier — have specialized in air-conditioning for the sensitized-products industry and will work out details for specific plants, but they must be called in *before* and not after the plans of a new plant are designed. As the humidity as well as the temperature must be carefully controlled, the air is usually taken from outside, after a preliminary filtering by a gauze that will remove gross mechanical dirt, and is pumped through a metal chamber in which large numbers of finely atomized water sprays are so set as to give as perfect contact with the air as possible. In an acid-laden atmosphere, the pH of the spray water may be kept slightly above 7, but ample washing with normal water is soundest practice. The washed air, more or less saturated, is now passed over cooling coils for which some form of refrigeration will be required. The expulsion of the water in the cold chamber, which is provided with baffles to assist the process, naturally lowers the temperature, and the cold, but now dry, air is led through a heating chamber where hot coils raise it to the temperature desired. Coating rooms may be conveniently kept at 70° F. (21° C.). Drying cupboards may be started at a few degrees above this, and gradually warmed up to 90° F. (32° C.), the heat being turned off a short time before the racks are collected. The design of the drying cupboards must be left to individual circumstances. They must be near to the coating machine, so that the racks of coated plates do not have to be carried too far. They should not be too big — a number of small cupboards capable of holding 500 or 600 8 by 10-inch plates each, is better than a few large ones. The racks are run on wooden rails in the cupboards, and both racks and rails must be of the smoothest possible character to avoid friction of any kind.

Assuming that the dust problem is solved by the use of water-washed air, the next most serious problem is that of bubbles. A tiny bubble may get lodged in the spreader and cause lines on

a large number of plates unless it is quickly seen by the coater and removed. Alcohol in the emulsion helps considerably in lowering the surface tension and reducing the tendency to bubbles. A small atomizer filled with alcohol, or a mixture of alcohol and acetone, is usually at hand to remove froth or bubbles. Careful filtering and skill in pouring and keeping the emulsion tranquil, are all helpful. Commercial specifics for lowering surface tension have been introduced in the trade and find useful application. Dull spots, often known as grease spots, sometimes appear on the surface a few seconds or minutes after coating, and a saponifying agent such as an alcoholic solution of saponin may be helpful.

A very even distribution of the air in the drying cupboards is essential, otherwise drying marks may appear which reveal themselves, on development, as local patches of uneven density. Any sudden change in the rate of flow of the air through the cupboards, will also cause drying marks or demarcation lines where the change took place. Some factories remove the racks when the plates are dry and place them in an *after-drying* cupboard for a few hours without ventilation and at an elevated temperature, such as 122° F. (50° C.). This is claimed³ to improve the keeping qualities and to be of especial value in the case of plates destined for use in tropical climates.

Before cutting and packing, each plate is briefly examined by looking through it at a safelight for bubbles, scratches or other defects. Glass-cutting machines are in general use for dealing with large sizes which have been coated for smaller ones.

Probably only those who have had to tackle the problem of coating plates year in and year out, are aware of the extraordinary diversity of faults which can develop in manufacture. Perfectly good plates may be spoiled by the use of unsuitable packing materials. Not only must the boxes be made of materials which have no deleterious effects — and the glue used is as im-

portant as the card itself — but the wrapping paper must be most carefully tested for its effects, if any, by oven tests. Ten days at 105° F. in an oven maintained at not above 65 per cent relative humidity is a fair test. The plates so “incubated” should show no more than 0.02 extra fog density when compared with controls, and given normal development. The card separators used for keeping each pair of plates from touching, or for grouping each pair together, must also be made from card which has passed the laboratory test. Even outside labels require to be free from contaminating power, as also any slips or literature which may be packed inside the boxes.

It is of course most important to keep a record of batch numbers, and a serial number given to the box, checking with the emulsion laboratory records, will enable complaints or faults to be investigated.

Chapter References

1. L. P. Clerc, *Photography*, p. 157.
2. T. L. Dixon and Co., Ltd., Letchworth, England.
3. R. Jahr, *Fabrikation der Trockenplatten*, p. 236.

CHAPTER IX

BROMIDE AND CHLORIDE PAPERS

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

WHILE natural-color photography has re-introduced to a limited extent the transparency picture, which is viewed by transmitted light or by projection, the natural desire in taking a photograph is to have it finally in the form of a print which can be viewed by reflected light. Some form of print is indispensable in any case, if the original takes the form of a negative. A print on any photographic paper is of course also a negative, for printing a negative from a negative reverses the image and produces the positive picture. Certain losses occur in the process, but modern sensitometry has gone a long way towards reducing them to a negligible minimum.

One function of the print is to provide, in fact, some means of control over the negative image and its possible shortcomings. If a negative is too hard, we can use a soft-working paper; if the negative be flat, we can print it on a vigorous paper, and so on. The most practical example of the application of this control is seen in the work of the photo-finisher, who uses perhaps four different grades of paper in making prints from customers' negatives, soft, medium, vigorous and contrasty. By selecting a paper for each negative merely by means of an experienced eye, and taking each print out of the developing solution at the right moment, a remarkable uniformity of quality is obtained in the prints from a range of negatives that, without such facilities, would be almost impossible to deal with.

One of the most important factors in the making of photographic papers is the paper base. The production of a permanent image, provided the paper is handled in a proper manner, is a moral obligation on the part of the manufacturer, and with this in view the testing of the raw paper becomes essential. The manufacture of very pure, strong papers of close texture, durability and uniform weight suitable for emulsion coating, is in the hands of a comparatively few firms, and is a highly specialized department of the art of paper making, of which the literature is somewhat scant. Quality of water has in many cases been a deciding factor in the success of a photographic raw paper undertaking. The paper is ordinarily made in rolls 42 to 44 inches wide, in 500-meter lengths in the card thickness, and 800- to 1000-meter lengths in the lighter weights. A square meter of light-weight paper will weigh 90 to 135 grams, card thickness 210 to 270 grams, while various medium heavy weight varieties come between the two.

The paper must show a uniform texture when examined by transmitted light, and it must not stretch too freely when wet, nor shrink too much when dried after wetting. For this reason papers containing much wood pulp are unsuitable, and a test for wood fibers is usually one of the preliminaries in connection with an unknown sample. The following solution may be used for the test:

Alcohol	100 cc
Phloroglucin	2 g
Hydrochloric acid	50 cc

This solution, freshly prepared, is of a weak yellow color. Its application to the paper sample will cause wood pulp or fibers to turn red. Another useful test is that suggested by Herzberg;¹ a solution of twenty grams of zinc chloride in ten cubic centimeters of water is mixed with five cubic centimeters of

water containing 2.1 grams of potassium iodide and 0.1 grams of iodine. The solution is shaken up, allowed to stand, and the clear portion decanted and used. A sample of paper which has been pulped by boiling with a five per cent solution of caustic soda for a few minutes and well washed is treated with this solution, which shows rag fibers as deep wine red, starchy substances as blue, and wood fibers as yellow.

Impurities in the raw paper come into evidence most frequently in the form of small spots, which may develop in size when the emulsioned material is kept for any length of time before use. Iron particles probably cause the most trouble. These can be checked by soaking a sample of the raw paper in a dilute acidified solution of the ferricyanide and ferrocyanide of potassium for five or ten minutes and then washing with distilled water. The presence of iron will cause a blue coloration; low-power microscope examination may be needed to detect small specks. The paper may otherwise be soaked in a one per cent solution of pure nitric acid, dried, and then transferred to a dilute solution of potassium ferrocyanide; in this solution copper spots will be revealed as brown marks or stains, iron spots as blue. Needless to say, photographic raw papers should be practically free from loading.

Paper is used in the raw state only where a natural surface is required. Otherwise a coating of baryta is applied to the surface to be emulsioned. A mixture of barium sulphate and gelatin, with a suitable hardening agent, is applied to the surface with reciprocating brushes. In a glossy paper about ten parts of medium hard gelatin would be used to one hundred parts of fine baryta; in a mat paper, the proportion of gelatin has sometimes to be raised, on account of the heavier baryta used. Some kaolin may be included. An addition of glycerin, chrome alum (or formalin), and some citric acid usually, together with a small amount of coloring matter, completes the

mixture. Red, yellow, or blue dyes are most popular, but the baryta never looks a good color without *some* dye. A typical baryta coating machine ² is seen in Fig. 45. The baryta mixture

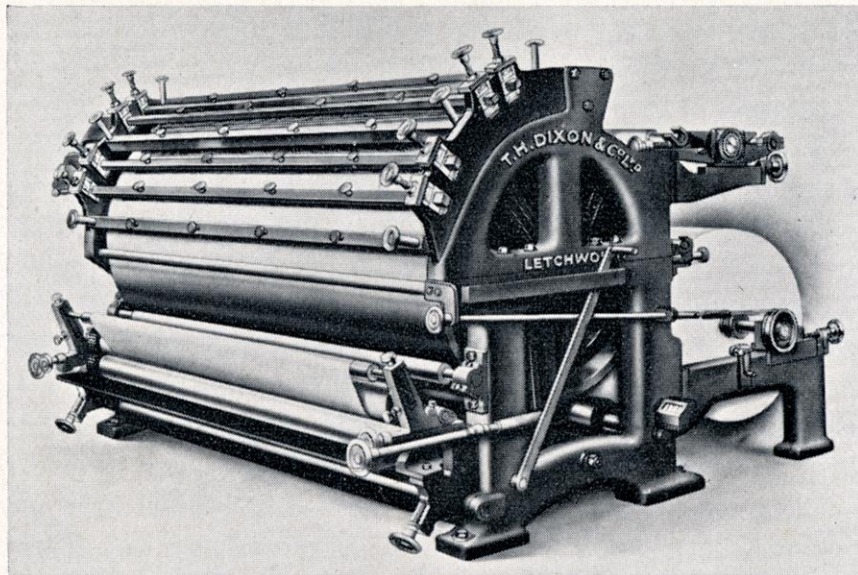


FIG. 45. BARYTA COATING MACHINE

is applied to the paper, which after leaving the machine is run into loops, the festoon traveling along a drying tunnel which is maintained at a controlled temperature and humidity. It is reeled at the end of the run, and is afterwards passed through a calendering process, where it is burnished and given the necessary finish by its passage through highly polished rollers under considerable pressure. According to the baryta formula used and the calendering treatment, the surface produced may be glossy, semi-glossy, half-mat, full mat, or rough mat. The baryta coating keeps the emulsion on the surface of the paper, so that the image lies superficially and is therefore more brilliant. This incidentally makes the emulsion go much further.

Practically all development papers are given a non-stress coating, to prevent abrasion or pressure on the emulsioned surface from causing black marks or streaks. Pressure will cause the film to become developable without exposure. The non-stress coating is a thin application of plain gelatin coated over the actual emulsion, and in modern practice is applied as soon

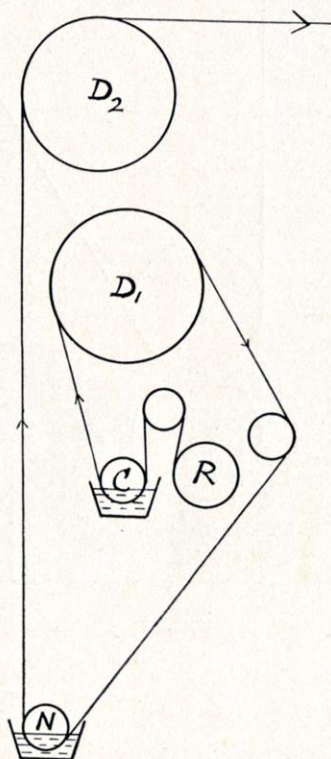


FIG. 46

as the emulsion itself is thoroughly set. The method of applying the two coatings on a double coating machine is seen diagrammatically in Fig. 46. The mechanism for forming the loops is not shown. The raw paper from the roll *R* is led over a roller *C* which dips into a silvered trough kept filled with

emulsion at constant level. As the paper is driven forward it touches the emulsion and picks up a quantity which varies with the rate of travel, which may be anything from twelve to fifty feet per minute. The paper, with its emulsion coating, is led over a large-diameter cold metal drum, D_1 , where setting takes

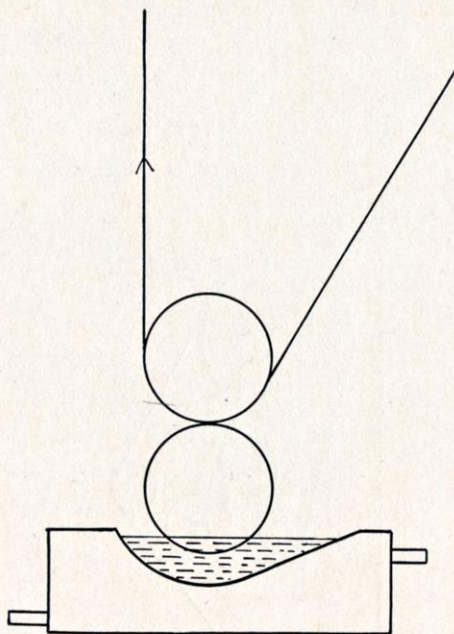


FIG. 47

place, and it is then led over guide rollers to a second coating trough where the non-stress gelatin is applied by the roller N ; this is set in turn by the second cold drum D_2 . Both coatings can be applied by "kissing" rollers (Fig. 47), instead of by dipping. An advantage of the kissing roller is that it can be made slightly shorter than the width of the paper, so that an uncoated selvedge is left at the two sides on which the leading rollers over the setting drum can ride. In the case of dipping, the emulsion is necessarily applied to the entire width of the

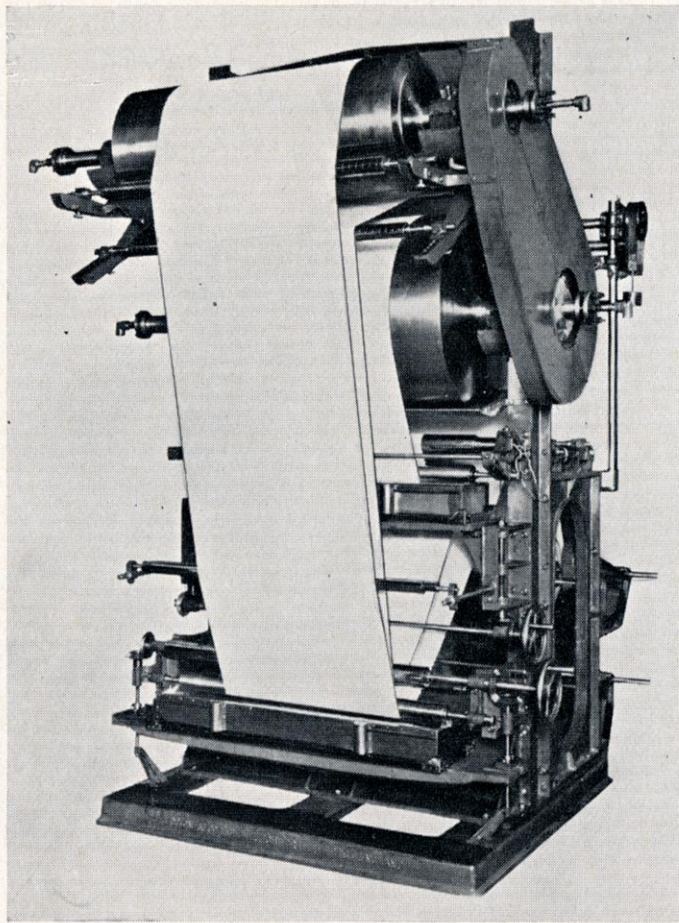


FIG. 48

roll, and if clear edges are needed for leading rollers, a scraping device must be attached to remove the emulsion for about half an inch at the two sides.

By simple mechanical means, the coated band, thoroughly set by the second cold drum D_2 , is picked up and formed into loops eight or ten feet long, which depend from sticks that are carried along by endless sprocket chains running along the top of the drying alley. The festoon thus travels slowly down the

alley or tunnel, which may be 200 or 300 feet long. Frequently it is made double, so that loops are carried on the sticks over a turntable at the far end of the tunnel and then travel up again, so that the paper is dry by the time it has reached the *reeling*

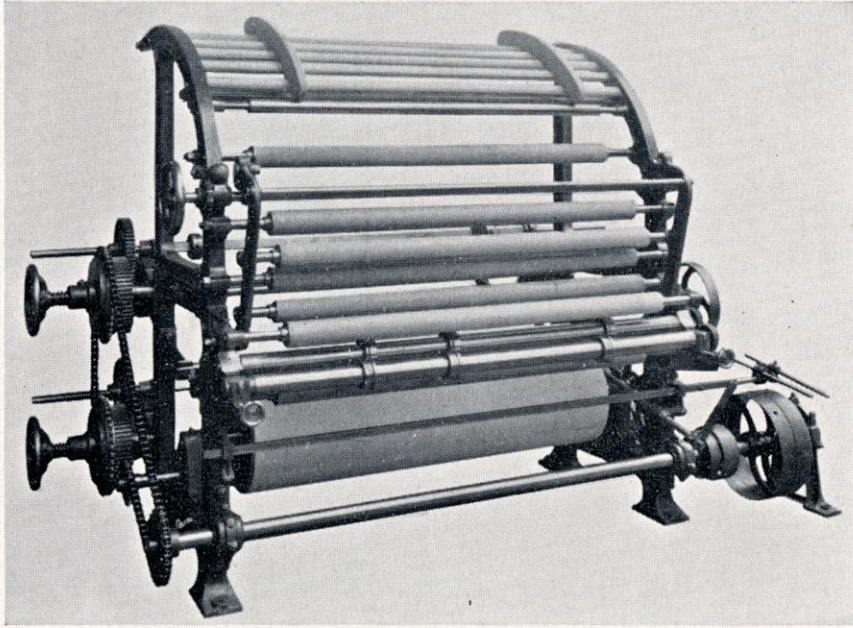


FIG. 49

machine at the coating head end of the building. A double coating machine made by T. L. Dixon and Co., Ltd. is seen in Fig. 48. New rolls of paper can be attached to ends of finished rolls by means of auxiliary gear, so that coating can be continuous. In Fig. 49 is shown a reeling machine made by the same firm; the paper is led in and out of the tension rollers to smooth out irregularities and creases before being wound on the drum.

With a little skill, a very good coating of paper can be obtained in the laboratory with just a dish of emulsion standing in an outer dish of warm water, laying a short, loosely rolled-

up length of paper three or four feet in length on the surface, and pulling it vertically upwards with a quick, steady movement (Fig. 50). The roll of paper will lie on the surface and

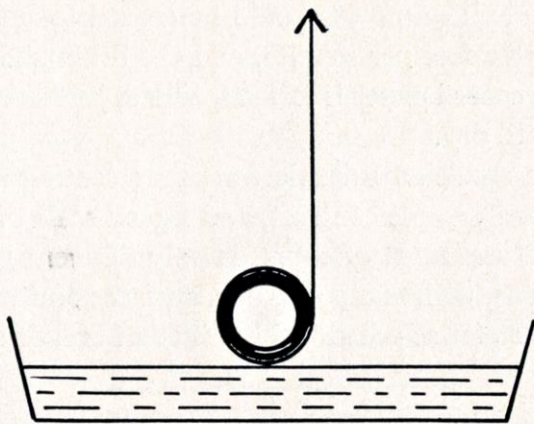


FIG. 50

as it unrolls the action will be substantially the same as that of a dipping machine. If longer lengths are desired, a somewhat elaborated arrangement can be used as shown in Fig. 51. This can be made with a little mechanical help, and indicates a homemade paper-coating machine. A roll of twenty feet or so of raw paper is wound on to a wooden roller the spindle of which is supported by two uprights, one on either side of the coating dish. The dish is filled with emulsion just before coating so that the bottom of the roll dips about one-quarter inch below the surface. The paper to be coated must be attached to a paper "leader" which travels upwards to the roller R_1 which should be fixed as high up as is convenient. It then passes across to a second roller R_2 and down again to a fourth roller or drum on which the coated paper is to be wound. A small motor geared to this drum will drive the paper, and the leader will draw the coated paper over the upper rollers and

down to the drum, when of course coating must be stopped. A length of about twenty-four feet can be coated at one time in this way in an ordinary room, the length depending on the height of the leading rollers above the dish and the distance between them. The motor should be geared to run the paper at ten or twelve feet per minute, and the drum should be belt driven. The coated paper is left suspended, just as coated, over the rollers until dry.

A bromide emulsion suitable for paper coating should give pure black tones, ample contrast, and a good scale of gradation. The manufacturer must of course supply different grades from soft to vigorous, with many different surfaces and weights, and must arrange as far as possible that different brands of the same

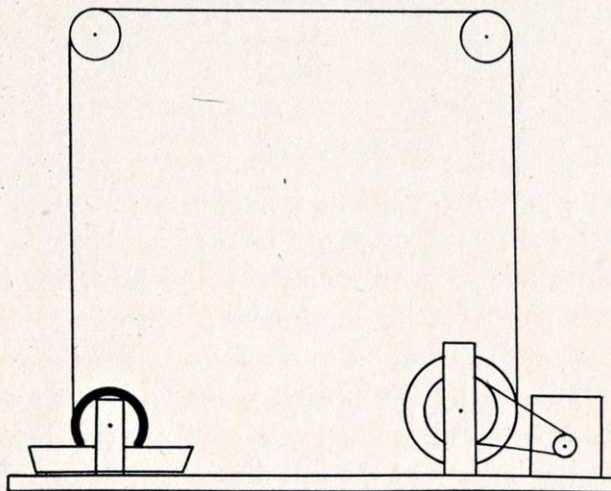


FIG. 51

class have approximately even speeds. Actual speed is of little consequence in a bromide paper, except for enlarging purposes or automatic printing machines, and even then it is of an entirely lower order as compared with negative emulsions. But it is nevertheless important to keep the speed of the different

grades uniform, and this will be found to be by no means as easy as it might seem.

For laboratory or experimental work, the most important thing to be done is to get hold of some raw paper, and here one must depend on the courtesy of one of the manufacturers themselves, who in general do not discourage amateur efforts. Some photographers will wish to coat paper of their own choice in order to secure some particular surface. Use pure rag paper, unsized, such as Rive's or Whatman's. Thick papers are more difficult to handle than thin ones, and may have to be sensitized by floating on the emulsion one sheet at a time in an open dish.

When dealing with paper emulsions, useful information can be obtained by trial coatings on glass. This will show if the emulsion is free from fog, which should not exceed 0.02 density on normal coating, also if it has good latitude and has ample density-giving power. One hundred grams of silver halide will coat eighty to one hundred feet of forty-two inch paper.

The reflection densities of a sensitometric strip depend so much upon the paper surface and its absorption and diffusion qualities that a more *practical* indication of printing characteristics will be obtained from the coated paper. For information, it will be advisable to coat three or four strips say three feet long by eight inches wide, trying to keep the speed of unrolling on the emulsion constant. Each strip may be coated at a different temperature or a different speed to obtain the effect of varying coating weight. The faster the paper is unrolled, or the lower the temperature of the emulsion, the thicker will be the coating. Any form of strip sensitometer or gray step-wedge can be used in an ordinary printing frame for making the tests, but results can be charted as characteristic curves only by use of a reflection densitometer such as is described in Chapter XII.

It is all-important that the coating weight of a paper be correct within reasonable limits. Thus, while negative emulsions

are usually made with forty to fifty grams of silver nitrate to the liter, paper emulsions would be prepared with only fifteen to twenty-five grams per liter. This, of course, assumes that the actual volume of liquid emulsion applied to a given area is of the same order. One liter of emulsion should coat sixty to eighty square feet of paper surface. The viscosity of the emulsion, the surface of the paper, the coating temperature, and the speed of the machine will control coating weight. When dipping, the emulsion picked up is almost directly proportional to the peripheral speed of the coating roller. Good blacks can be obtained only if the coating is sufficiently rich, but too heavy coating is decidedly detrimental. It must be remembered that in the case of a transparency, density and contrast can both be built up over a long range, but in the case of a development *paper* the maximum contrast is attained very early during development, simply because the number of densities that can be distinguished by reflected light from the maximum black is extremely limited. This disadvantage renders it all the more important to limit coating weight to giving in the highest exposures the maximum density that is desired for the particular brand, this maximum to be measured after *normal* development. Brilliance depends on the gloss of the surface, and the contrast and cleanness of the emulsion, and can be largely lost if the latter sinks too much into the paper owing to lack of viscosity or too slow setting.

A bromide paper formula by Trumm is as follows:

A. Water	4000	cc
Gelatin	350	g
Potassium bromide	190	g
Potassium iodide	2.5	g
B. Distilled water	2000	cc
Silver nitrate	250	g
C. Water	2000	cc
Gelatin	600	g

The gelatin in *A* is allowed to swell in the solution of bromide and iodide for half an hour, and is then dissolved by heating the crock to 120° F. (49° C.). The silver solution, *B*, heated to the same temperature, is added, pouring it through a funnel with a fairly fine jet. A plain or separatory funnel can be used for the purpose, attaching to the end, by means of the shortest possible piece of rubber tubing, a 1 or 2 inch length of barometer tubing about 4 mm bore. The funnel is mounted in a stand above the crock so that the jet is near to one edge, leaving ample room for stirring (Fig. 52). The emulsion so made is next

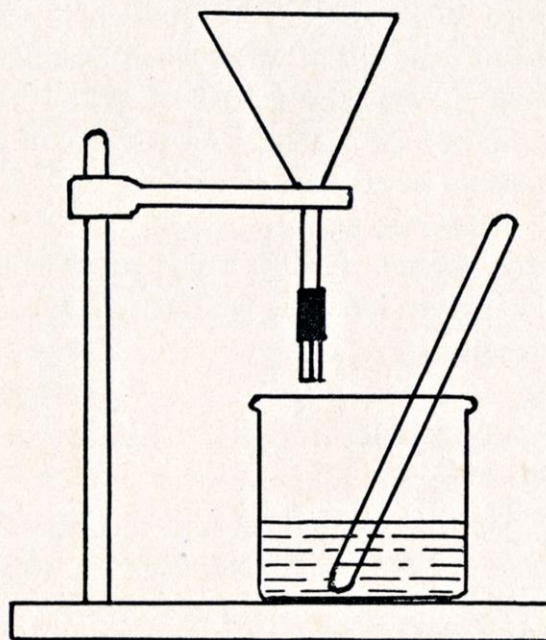


FIG. 52

further heated to 140° F. (60° C.) on a water bath, and maintained at this temperature for one hour. At the end of the hour, solution *C*, heated also to 140° F., is added, and a further one hour's digestion is given. The emulsion is then poured out to set in a cold crock placed in ice water and stirred slowly until

gelling begins. It is then broken up into noodles in the manner already described for fast emulsions, and washed in about twelve changes of five minutes each. The washed noodles are put into a tared crock, remelted and made up, inclusive of finals, to a weight of 16,000 g. Finals are:

Five per cent chrome alum solution	150 cc
Spirit	1000 cc
Phenol (dissolved in part of the spirit)	10 g

If a mat paper is required, 200 g of rice starch ground up in 1000 to 1500 cc of water is added and thoroughly stirred in, prior to filtering. When matting the emulsion, it is best to leave out an equivalent quantity of water when making-up. When made up to bulk, the emulsion is best set off and remelted next day or when required for coating. An addition of an alcoholic solution of saponin or extract of quillaia bark is frequently added to give better coatings.

An alternative formula for a bromide paper emulsion made with ammonia is given by E. J. Wall as follows. Three solutions are made up:

<i>A.</i> Water	1800 cc
Potassium bromide	400 g
Citric acid	400 g
Gelatin	150 g
<i>B.</i> Water	3750 cc
Silver nitrate	500 g
<i>C.</i> Water (cold)	600 cc
Gelatin	150 g

Solution *A*, the gelatin dissolved, is cooled to 86° F. (30° C.). To solution *B* is added sufficient stronger ammonia water to redissolve the precipitate. It is then added at the same temperature to *A*, through a jet, with continual stirring. The emulsion is then poured on to *C*, which is cold, and the whole stirred

and taken up to 122° F. (50° C.). As soon as the gelatin in *C* has melted, the emulsion is set. It is then washed as usual, the shreds melted and taken to 104° F. (40° C.) and 450 g of fresh gelatin is added which has been dissolved in 1600 cc of water. Final additions are 600 cc of alcohol and 30 cc of ten per cent chrome alum solution.

Unwashed emulsions have met with a limited amount of success for development papers. Inasmuch as too great an excess of free bromide would not only greatly retard development but cause the "blacks" to have a decidedly greenish tint, it is important that only a slight excess over the combining proportion should be used. Also, on account of the hygroscopic nature of ammonium nitrate, the potassium salt would be used. An unwashed emulsion would be acid in character, and could be made up somewhat as follows:

A. Potassium bromide	26 g
Potassium iodide	0.5 g
Potassium chloride	1 g
10 per cent hydrochloric acid	5 cc
Gelatin	30 g
Water	560 cc
 B. Silver nitrate	 37.5 g
Water	300 cc

Heat both solutions to 140° F. (60° C.), and add *B* to *A* through a fine jet with mechanical stirring. Digest for an hour and a half and then add 50 g dry gelatin, and stir for ten minutes until dissolved. Then add 50 cc of a two and a half per cent solution of phenol in alcohol, and 5 cc of five per cent chrome alum solution, and set off in ice water. Keep in cold room for three days. Remelt and filter.

Formulas already given for transparency emulsions can with some little adaptation be used for coating bromide paper. Papers requiring a long scale of gradation may be made with di-

vided silvers, using a small amount of ammonia only and allowing a little ripening time. Mixed jet emulsions give excellent results. In all cases, the choice of gelatin must be carefully made; slow emulsions are probably more dependent on gelatin character for their success than rapid ones.

The popularity of chloride papers, or "gaslight" papers as they are known in the English market, is due to the extreme ease with which they can be handled. The early papers of this type were so vigorous that for a time specially soft negatives were necessary to obtain the best results. Studies of the behavior of silver chloride, however, have made it possible to produce chloride papers giving a wide range of contrast. A simple emulsion suited to experimental work is as follows:

A. Sodium chloride	12 g
Gelatin	90 g
Water	1000 cc
B. Silver nitrate	25 g
Water	110 cc

Both solutions are heated to 122° F. (50° C.), and *B* is added to *A* either through a fine jet or in small quantities at a time — such as 10 cc. The liquid should be kept mechanically stirred at a high speed. Between forty and fifty minutes' digestion is given at the same temperature, and the finals are then added.

This is an unwashed emulsion, and as such is apt to attack the baryta surface with the formation of minute black or white spots. If the emulsion is washed, it may be used for coating either chloride paper or lantern plates. To the above quantity of emulsion an addition may be made of 5 to 10 cc of a ten per cent solution of citric acid, the lesser amount tending to give bluish blacks and the greater amount greenish blacks. Three or four cubic centimeters of a ten per cent chrome alum solution

and five per cent of the total volume of alcohol should be also added. An emulsion of this type is an interesting one to experiment with, since all the work can be done in the subdued white light of the darkroom. Works-scale chloride emulsions are handled in yellow light.

The brilliance of chloride and chloro-bromide papers can be increased by the discreet use of copper or thallium chlorides, although of most importance is the correct choice of gelatins. Small additions of citric acid, potassium citrate or sodium phosphate may be made to washed emulsions to improve keeping quality, and formalin may be substituted for chrome alum in the case of manufactured material which is destined to get some rough handling in photo-finishing shops. The amount of formalin used would be about fifty to sixty cubic centimeters of forty per cent formaldehyde diluted with ten times its volume of water, for every kilogram of gelatin. Where emulsions are to be washed, hydrochloric or citric acid is advisable in the making; hydrochloric would be added to the salts, but the citric acid may be divided between salts and silver.

Intermediate between chloride and bromide development papers there come, of course, the chloro-bromide variety, designed for giving warm tones. The formula already given for chloro-bromide plates can be used with very little modification. As a starting point for experiment, a mixture of equal parts of bromide and chloride might be taken. The silver halide concentration should be about twenty-five to thirty grams per liter, and the gelatin concentration about double this. The excess of soluble halide should be chloride, not bromide; the precipitation made in the presence of free acid as indicated for chloride emulsions; and after washing, only a trace of bromide should be used, otherwise the tones will tend towards a greenish hue. It has been the experience of some American emulsion chemists that halides of barium, cadmium and other metals give better

warm tones than those of potassium, sodium and ammonium. The inclusion in the emulsion of anything which will tend to restrain development may also help; the citrates and borates are examples. But in both types of paper, chloride and chlorobromide, the manufacturer has to correlate his emulsion coating with an optimum developer, the latter being essentially worked out for the material in question. Thus A's paper developed with A's formula might work excellently, while used with B's formula the results might be very poor.

Care must be taken to avoid froth and bubbles on the surface of the emulsion in coating. For laboratory experiments, the emulsion should be filtered just before use, through a piece of wetted cheesecloth, and poured down the side of the dish to avoid friction, holding the crock or beaker near to the dish. Large bubbles can be broken by the touch of a moist glass rod; froth can be dispersed by the cautious use of a little alcohol blown from an atomizer. Too much alcohol will cause the emulsion to coagulate in the form of little strings or flecks which must be removed.

The non-stress coating applied to the emulsioned paper in a double-coating machine, which is composed of gelatin, spirit, and some hardening agent, may suitably contain formalin, chrome alum being preferable in the sensitive emulsion. The double-coated paper takes somewhat longer to dry than paper which is not non-stress coated. It is important, for example, to arrange the inlets of air in the drying tunnel so that warm, dry air is blown gently into the loops from the sides of the tunnel, and that sufficient air is directed on the bottom of the loops, where drying is apt to lag. The amount of air required to be pumped into the tunnel — and it should be pumped in under slight pressure so as to form a plenum, and not merely *extracted* — will naturally depend on the temperature and relative humidity and on the amount of water to be evaporated

during the run from coating head to reeling machine. The inclusion of a small quantity of Arlex may be made in the case of continuous running, which acts as a plasticizer and is only slightly affected by changes in humidity; some coaters prefer to run the festoon to the end of the tunnel, and to leave the paper for some hours in a 50 per cent relative humidity atmosphere to get into equilibrium before reeling. This is only possible where comparatively small coatings are made.

A new type of bromide paper has recently been introduced which is capable of giving images of either high or low contrast according to the color of the light used in printing (Defender "Varigam" and Ilford "Multigraph"). These papers are coated with a mixture of two different emulsions, one sensitive to blue-violet only and having, say, a high gamma, the other sensitized to green by means of a suitable dye, and having a low gamma. The contrast obtained with the one paper can thus be varied at will by merely using the appropriate filters over the printing light or the lens of the enlarger, thereby bringing into requisition the emulsion required.

Some causes of failure with slow development papers may be given, in conclusion. Weak, grayish images may be due to the emulsion taking up too much water in washing, and hence causing a deficiency of silver. Low viscosity will give the same trouble. Gray images with a tendency to fog are usually due to over-digestion; the remedy is to reduce the time or the temperature of the cooking. An unsuitable gelatin may also be the cause. General fog may be due to an unsuitable gelatin, too high temperature for emulsification, insufficient excess of halide, impure chemicals, and, of course, too much exposure to light. Black fog indicates an excess of silver nitrate, due to incorrect weighing or miscalculation of a formula. Partial fog is sometimes caused in a mixed-jet emulsion through the silver leading the salts and not vice versa. Innumerable tiny black specks on

development, or pepper, are due to coarse precipitates or aggregates of silver halide which, being insufficiently clothed with gelatin, are reduced without exposure. These rarely occur with an ammonia type of emulsion, but are very apt to creep into chloride emulsions, having a serious effect on the brilliancy or maximum density. A cubic centimeter or two of the emulsion just after it has been made, should be spread over the end of a glass strip and examined by transmitted light, for example by looking through it at a low power incandescent lamp. The addition of the second gelatin dry instead of in solution, helps considerably to break up or disperse aggregates; finer nozzles for the silver, better agitation during precipitation, or an increase in citric acid, will help to prevent pepper formation, or again a change of gelatin or its distribution between salts and silver.

Chapter References

1. W. Herzberg, *Die Papierprüfung*, 1907.
2. T. H. Dixon and Sons, Ltd., Letchworth, England.

CHAPTER X

FILMS, NEGATIVE AND POSITIVE

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

THE film bases on which sensitive emulsions may be coated are of two kinds. One is celluloid or "nitrate" film, which contains about 85 per cent of nitrocellulose and 15 per cent of camphor, the two being dissolved in about five times their weight of a mixture of about 37.5 per cent of 85 per cent alcohol and 62.5 per cent of ether, to form the dope from which the base is cast. The other base is cellulose acetate film, which is practically non-inflammable, and is compulsory for sub-standard motion-picture film and is becoming used on a very large scale for general photographic materials. Cellulose diacetate is made by heating cellulose with zinc acetate solution and treating the cooled mass with acetyl chloride. It is dissolved chiefly in acetone, to which a plasticizer such as triphenyl phosphate, dibutyl phthalate, etc., is added, together with tetrachlorethane, methyl alcohol or benzene. The recent introduction of triacetate in place of diacetate produces a tougher film, though the use of a special substratum is indicated.¹ The mixed dope is filtered through filter presses, and is generally fed by gravity from an upper mixing room to the casting machines.

The dope is cast into the thin sheet used in film coating by two different methods. One of these is known as the big wheel

system; the dope is distributed by means of a spreading device on to the flat periphery of a large highly polished metal wheel or drum which may be sixteen to twenty-five feet in diameter. The drum rotates at the rate of two or three feet per minute, and as it revolves the dope solvent evaporates and leaves the film sufficiently dry towards the end of the revolution for it to be parted from the metal surface and led into a drying chamber; here the remaining solvents are driven off, after which the band of film can be reeled. Much film base manufactured today is cast on an endless band type of machine. By this method, a band of copper about ninety feet long travels slowly over two large drums some three feet in diameter and spaced about forty feet apart; the whole is encased in a metal cover so that the evaporated solvent can be collected and condensed. Over the top of one drum is the spreading device, from which the dope is distributed on to the band. The band itself, however, is usually coated with a skin of gelatin, glycerin and soap. By the time the coated part of the band reaches the end of the run it is dry enough to be parted from the skin, and can then be passed through a final drying chamber and the residual solvent driven off. In the case of triacetate film the base is sometimes given a treatment before being finally dried, which acts as a substratum and anchorage for the emulsion, thereby doing away with the need for the application of a substratum in the emulsifying plant.

In the ordinary way, both celluloid and cellulose acetate require a preliminary treatment to secure satisfactory adhesion of the emulsion to the base, a problem that has involved considerable research to find a satisfactory solution. It will incidentally be found one of the most troublesome parts of the technique in laboratory coatings. The function of the substratum is to etch and attach itself to the film base on the one hand, and to "stick" to the gelatin of the emulsion on the other. The sub-

stratum most commonly used in early practice was thus a solution of gelatin in a solvent such as acetic acid or salicylic acid broken down with methyl alcohol. Ten cubic centimeters of glacial acetic acid may be put in a test tube and powdered gelatin added gradually, warming the tube gently over a Bunsen burner or alcohol lamp until no more gelatin will dissolve. This stock solution can be diluted with 200 cubic centimeters of methyl alcohol, to which two or three cubic centimeters of water has been added. This substratum works well with celluloid, but if it is to be used for acetate film, a part of the alcohol should be replaced by acetone. Five per cent of cellosolve acetate may also be added.

For cut sheet film Wall ² recommends the following:

Pyroxylin	0.5 g
Gelatin	0.5 g
Glacial acetic acid	33 cc
Methyl alcohol	1000 cc

The gelatin and pyroxylin are dissolved in the acid by heat, and the alcohol then added. The drawback to an acetic acid substratum is that it may lower the pH of the emulsion in contact with it and gradually slow it down, or affect color-sensitizing dyes. An alcoholic solution of caustic potash, to which a small proportion of celluloid solution (celluloid clippings in amyl acetate) is added, is dangerous from the opposite standpoint. Some of the recently introduced compounds of the Carbide and Carbon Chemical Corporation's research department have the advantage of giving a "tooth" to the film by slightly etching the surface through their mild solvent action. Cellosolve acetate is one example. The methyl compound is ethylene glycol monomethyl ether acetate, is miscible with alcohol, soluble in water, and soluble in cellulose acetate dissolved in acetone.

An organic partial solvent, suitably diluted, can be used to give a front etch for adhesion and a back etch for anti-curl

purposes. In some cases the film base is first coated with a thin application of hardened gelatin to offset the curl imparted by the emulsion. This balance is very important, as otherwise, during development in filmholders, cut film would curl and drop out of the grooves, while rollfilm would be unmanageable after

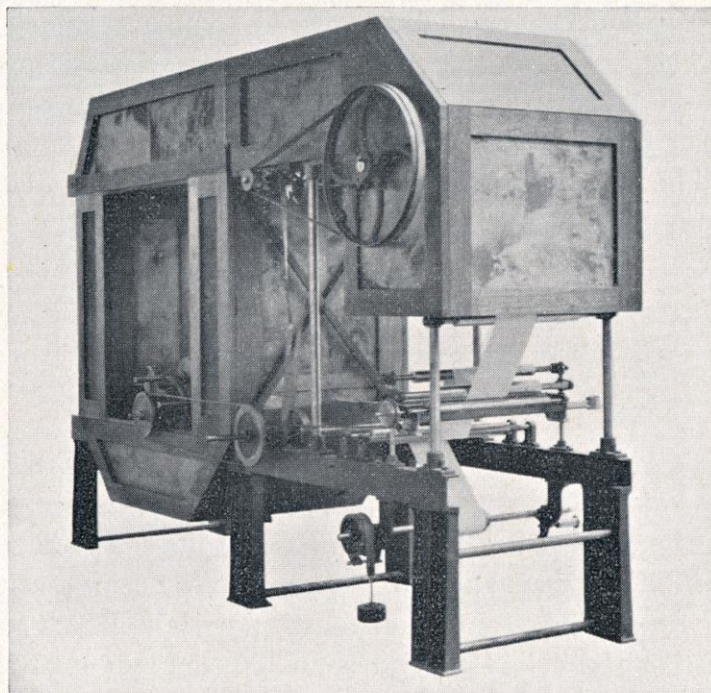


FIG. 53

processing. Too deep an etch will of course give an opalescent appearance to the film, although this disappears if a coating of gelatin or emulsion is applied afterwards.

Any form of substratum must be applied in a dust-proof alley or chamber of carefully controlled temperature and humidity. The average application should dry in three to five minutes at a fairly high temperature such as 95° F., so that the roll of film

base can be run continuously and reeled up at the end of the machine. It should be rolled up on large drums in order to make the base lie flat when running through the emulsions machine. A large inverted U-shaped substratum machine much in use is constructed by Koebig of Radebeul, Dresden, but a more recent form of apparatus is shown in Fig. 53, a compact subbing machine made by T. H. Dixon of Letchworth, England.

In substratuming base for special purposes, a coloring matter is sometimes introduced, as in the lavender motion-picture film of the Eastman Kodak Company, and the "gray base" film. The latter is claimed to give negatives of better quality, without interfering with gradation. The coloring matter, being incorporated in the water-insoluble base material, will obviously not be removed in processing. While therefore some anti-halation dye may be used, it will be necessary to resort to a dye in the back gelatin coating if such dye would interfere with the printing qualities of the finished negative; dyes which can be eliminated in an acid fixing bath etc., have been referred to on page 80.

Owing to dirt which inevitably creeps in during manufacture, transit, and general handling, the film base may be wiped or cleaned prior to subbing, by passing it through tightly coupled rollers or pads covered with suitable material. The cleaned and substratumed film base is coated at a fairly rapid rate — anything up to forty feet per minute — and after the application of the emulsion, it is passed over a large copper drum filled with chilled water which sets it sufficiently for it to be carried over on rollers to a mechanical festooning device which forms the band into loops depending from sticks as in the case of paper coating. The loops will be shorter and wider, owing to the nature of the base as compared with paper; loops five feet deep are customary in the heavier weights, and longer loops in the case of 5/1000 and 3/1000 base. The festoon travels along the

drying alley or tunnel, which should be constructed with ceiling, walls, and floor, of concrete or similar material sufficiently surfaced that when hosed down no dirt can remain on them; side gutters should be rounded off so that there are no "corners" to trap dust. Needless to say, both temperature and humidity must be controlled, and the circulating of the washed air so arranged that the bottoms of the loops dry in the same time as

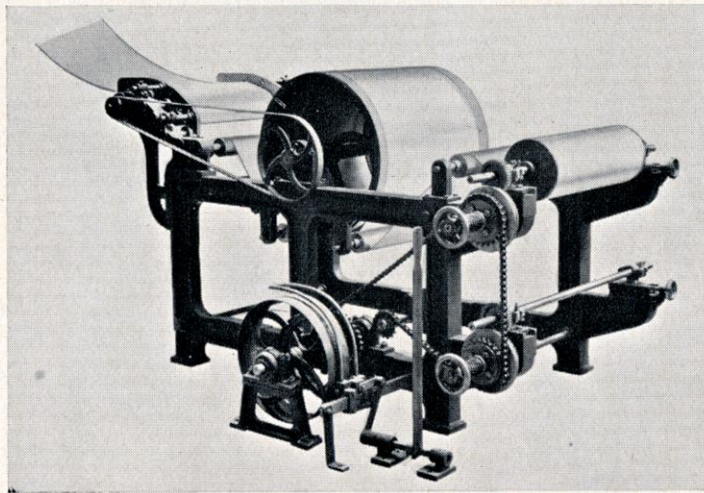


FIG. 54. REELING MACHINE

the lengths. With a drying alley 300 feet long, that is 600 feet run if the alley is double width with a turntable at the far end, the film should be easily dried by the time it reaches the end of the travel, so that it can be reeled and the coating process thus made continuous. A typical film reeling machine (Dixon) is seen in Fig. 54.

Coating small quantities of film in the laboratory or in the darkroom has naturally to be done on an entirely different basis. For short coatings on an improvised machine, lengths of ten or twelve feet of the $3/1000$ -inch thickness are recommended. If,

however, cut film is wanted, the $5/1000$ or $7\frac{1}{2}/1000$ -inch base may be cut into sheets on a clean print trimmer, and individual sheets squeegeed down on to "stickybacks" — glass plates prepared with a non-drying gelatin mixture. A small machine can be made quite easily in the manner indicated in Fig. 55. A cou-

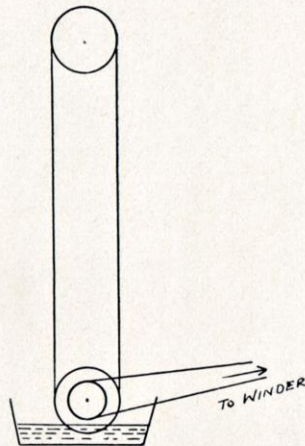


FIG. 55

ple of 10 or 12-inch rollers, turned true and polished in the lathe, of about $2\frac{1}{2}$ inches diameter, are mounted on spindles running in ball bearings fixed in the two uprights shown screwed to the base. The rollers should be given two or three coats of shellac varnish. The distance between the upper and lower roller, of course, controls the length of film that can be coated, as it is fitted over the rollers in the form of an endless band. It is a convenience if one of the rollers can be adjusted in the vertical direction so that the band when fixed can be pulled taut. While film cement may be used for making the join, a piece of one-inch scotch tape will answer the purpose quite well. The lower roller is the "coating roller," the dish of emulsion being brought up to it so that the film dips into it about one-quarter inch; the emulsion dish should be stood in an outer dish of hot water.

182 PHOTOGRAPHIC EMULSION TECHNIQUE

While the little machine may be driven by means of a handle connected by a belt to one or other of the rollers, it may equally well be operated by a large driving wheel, belt-driven from a

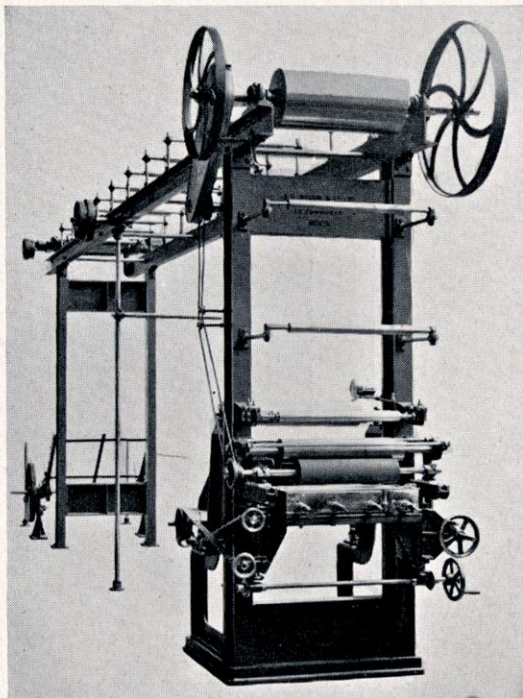


FIG. 56

slow speed motor having a very small diameter driving wheel. The speed of running should be about twelve feet per minute, using a viscous emulsion at a temperature only a few degrees above the setting point. In many commercial machines the band of film, after dipping, is run almost vertically upwards through a rectangular-shaped cold shaft, fitted internally with brine pipes, so that the surface of the emulsion is set by the time it reaches the cooling drum above it. This drum, which is usually of copper with cold water circulating through it, will

cause trouble from condensation and consequent buckling of the film unless continually wiped with a crossbar covered with absorbent material, or unless other equivalent steps are taken. While the pull of the drum may suffice to drive paper forward, film base requires some assistance, and either small weighted

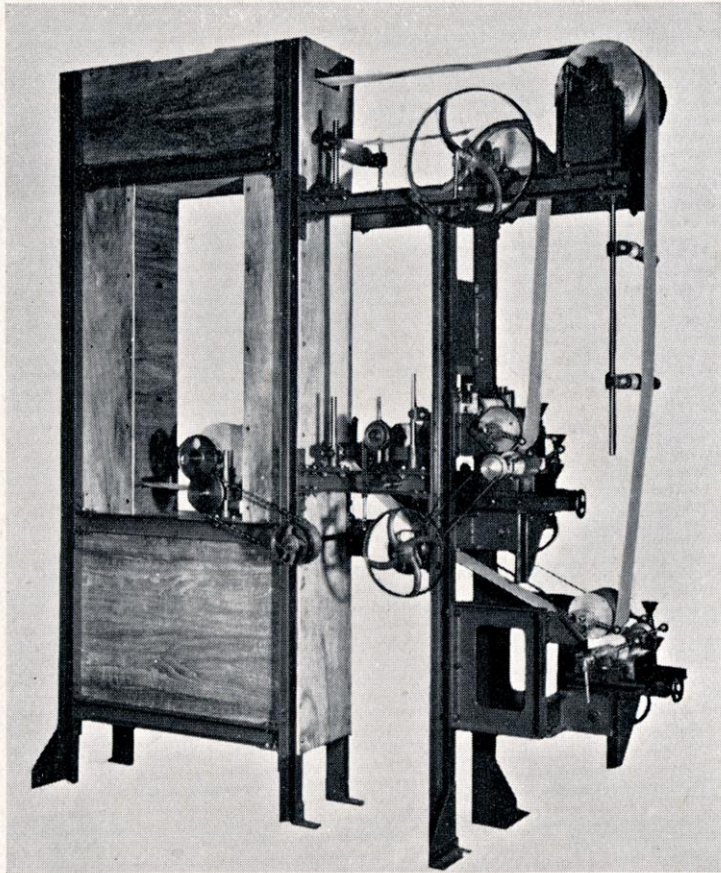


FIG. 57

wheels may be fitted at the edges of the band, to ride on the selvages, or a suction roller or belt may be applied immediately behind the drum. Suction rollers are used in many industries and can be obtained from a number of American manufacturers.

The roller is perforated, and suction is applied through the hollow shaft by means of a small motor-driven pump; the film clings to the surface under the vacuum and the rotation of the roller pulls it forward and feeds it on to the festoon.

A small laboratory coating machine³ is shown in Fig. 56, with which the film as it is coated is led by a leader of waste film or paper over the top rollers and down to the reeler. An elaboration of the machine, as manufactured by Dixon, is shown in Fig. 57, where arrangements are provided for double coating. Double coating is used on an increasing scale, and has many advantages. By coating an extreme-speed emulsion on top of a slower type, greater latitude is given and better building up of the image can be obtained, with increased densities in the highlights. Each coating must necessarily be of a lower coating weight than in the case of single coatings; halation is lessened, and by dividing the characteristics between the two layers, a film of improved keeping quality is produced.

Heavier base, the $7\frac{1}{2}/1000$ -inch, is the weight most easily coated in the laboratory in small quantities. It may be cut into sheets of a convenient size, say eight by ten inches, and stuck down on sheets of prepared glass, which are then dealt with exactly as dry plates. The celluloid or acetate base should be first substratumed on the side which is to be coated. The "sticky-back" glass is made by coating it with such a solution as the following:

Hard emulsion gelatin	60 g
Sugar syrup	60 g
Glycerin	80 cc
Ten per cent chrome alum solution	5 cc
Water	800 cc

About forty grams of Arlex⁴ may be substituted for the glycerin.

The gelatin is swollen in the water in the usual way, then

melted and brought to a temperature of 122° F. (50° C.) and the other ingredients added. Fifty to sixty cubic centimeters of this mixture will coat a sheet of glass eight by ten inches. Another formula for the sticky dope is as follows:

Hard emulsion gelatin	75 g
Arlex	30 g
Sugar syrup	60 g
Dextrin	20 g
Water to make	1000 cc

The gelatin is swollen in 700 cubic centimeters of the water, and is then melted and the sugar and Arlex added. The dextrin is mixed into a smooth paste with water, then thinned down with the balance of the water and heated until it forms a paste. This is mixed in with the gelatin solution, and if needed a little spirit can be added. The filtered material in either case is coated on the glass sheets in the manner of an emulsion. The plates should be given ample time to set, three to five minutes being necessary, and they may require two or three days to "dry." The large amount of glycerin or Arlex keeps the coating always tacky.

A sheet of sticky glass is taken, and a sheet of celluloid, substratumed side up, is slightly curved into a U-shape, convex side downwards, and lowered until it touches the middle of the plate. The two ends are then gently lowered, and with a flat squeegee the sheet of film is brought into firm contact with the tacky surface. The squeegee should be one made of black rubber. A wooden roller coated with billiard cloth or piano felt may be used instead.

In coating such films with emulsion, the inherent disinclination of all film base to take kindly to gelatin makes its distribution and adhesion difficult. Hence, while the plate is balanced on the finger-tips as has already been described in connection with dry-plate coating, it may be necessary to lead it over the

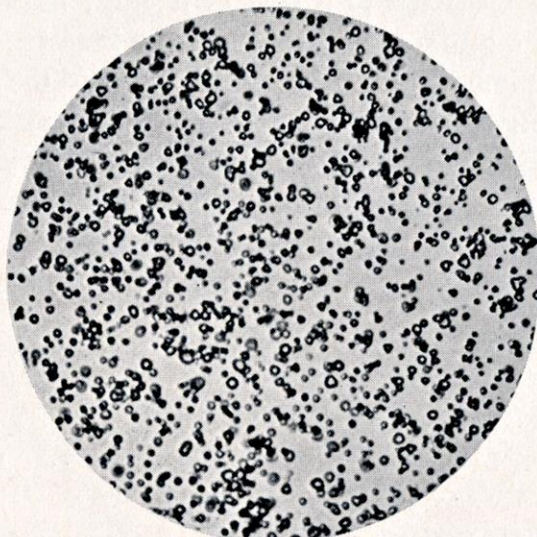
surface with a clean, warm, glass rod about a quarter inch in diameter held parallel to the glass, then carefully laying it on the levelling slab. Owing to the heat-insulating effect of the film base and thick gelatin coating, setting will be slower than in the case of a straight emulsion on glass, and this extra time must be borne in mind.

The coated films are dried on the glass in the drying cupboard in the ordinary way. When dry they are stripped off. Here a word of caution is necessary. One corner should be raised with a clean knife or spatula and taken between the thumb and finger. Holding the plate at the edges with the left hand, on which a cotton glove should be worn, the free edge is taken between the thumb and finger of the right hand and the film gently but firmly pulled away from the glass, taking care always that the plane of the film makes as acute an angle as possible with the glass. The film must never be pulled up vertically or backwards, or it will show stress marks. Too rapid peeling, or the use of any force, or any stop made during the stripping, may produce a static electric charge or a stress, which will appear as a fog mark on development. Buckles in the film show up on development, and are known as swallow marks.

The film should always be coated a little bigger than the size required, so as to provide space for trimming. In trimming, it should be remembered that cut film is about two millimeters less in width and length than the quoted commercial size. Thus in cutting a 4 by 5-inch film, the size would be made about $3\frac{2}{3}\frac{9}{2}$ by $4\frac{2}{3}\frac{9}{2}$ inches, otherwise it will not fit readily into the film sheaths or holders. The cut sheets may be packed emulsion to emulsion, each pair being wrapped in its own black paper folder. The black paper should be of approved quality and thoroughly dry.

Any emulsion may be used for film coating, but as already

indicated it should be of more viscous character than is needed for plate coating. A suitable gelatin for film emulsion is quoted by Heyne as one which requires forty-five seconds when made up as a two per cent solution to flow through the Ostwald viscometer. The same author suggests for a negative film emulsion



Courtesy DuPont Film Manufacturing Corporation

FIG. 58. MOTION-PICTURE POSITIVE EMULSION GRAINS X 1000

a formula which has been already given on page 68. The problem of keeping quality is somewhat more complicated in film production, on account of the character of the base itself and the substratum employed, and the alteration already mentioned as possible has been prevented to a large extent by the provision of an inert hydrophylic colloid buffered at substantially the same pH as the emulsion, or by treatment of the emulsion itself. Details of the more rapid types of panchromatic emulsion for film coating will be found in Chapter XIV.

A positive emulsion suitable for motion-picture work must

have a small, uniform grain and possess the necessary qualities for both sound and picture reproduction. A fine-grained, long-scale emulsion is needed for both positive and negative sound records. While commercial positive gamma is usually in the neighborhood of two, it must be remembered that the sound is ordinarily restricted to a part of it only; negative gamma ranges from 0.5 to 0.9, and the exposure is so regulated as to keep the maximum value below the shoulder of the characteristic curve. Fig. 58 shows a smear of commercial positive motion-picture emulsion at $\times 1000$ magnification and indicates the extremely uniform grain, which is nevertheless coupled with a long straight-line portion of the curve.

A formula for a positive emulsion is as follows:

A. Gelatin	400 g
Distilled water	2500 cc
B. Potassium bromide	400 g
Potassium iodide	15 g
Water	1500 cc
C. Silver nitrate	500 g
Distilled water	1500 cc
D. Gelatin	350 g
Water	1000 cc
Ammonia (s.g. 0.910)	45 cc

This is a mixed-jet type, so that *B* and *C* are poured through five- to six-millimeter nozzles, at temperatures of 140° F. (60° C.) and 77° F. (25° C.) respectively, into the crock containing the emulsifying gelatin *A*, which should be at about 120° F. (50° C.). The emulsion is digested at 120° F. for thirty to forty-five minutes, and is then poured into *D*, which has been previously heated to the same temperature. The emulsion may be further digested after washing if the tests show it to be necessary.

An all-ammonia positive film emulsion may be made as below:

A. Water	1200 cc
Ammonium bromide	150 g
Ammonium iodide	4 g
Soft gelatin	120 g
B. Water	100 cc
Silver nitrate	200 g
Ammonia to redissolve.	

Half the silver is poured at 77° F. through a nozzle or jet into the crock containing the A solution (at 105° F.); the other half is then "flopped" in without stirring, and 200 grams of dry, high-viscosity gelatin is then added and stirred in until completely dissolved. The emulsion is maintained at 105° F. or just under, then set in ice water. It is very thoroughly washed in order to get rid of all the ammonia, and made up with spirit and finals to 4000 cubic centimeters. Coating weight should be 90 to 110 milligrams per square decimeter.

In view of the increasing interest in the making of color prints by the wash-off relief process, and by superimposition of three dyed gelatin images on film base, some description of the materials used should be given. The original idea of using gelatin reliefs as matrices for producing the elements of a subtractive transparency must be ascribed to E. Sanger Shepherd, to whom the Progress Medal of the Royal Photographic Society was awarded for this work nearly forty years ago.

A wash-off relief film can be used in two ways. One way is by sensitizing a slow gelatino-bromide emulsion with dichromate, exposing it through the back of the film and developing it in hot water; the washed-out relief image is fixed and washed, when it can be used to imbibe the necessary dye, which can be transferred to paper or left in the film if the latter is to be made one element of a three-color transparency. The other way is to expose the film under a negative and after developing it to

harden the image with a bleaching bath, so that on treatment with hot water the exposed image alone remains, with its tone scale duly represented by graduated thickness of the gelatin relief. This may be used as a matrix for taking up the necessary dyes, which can be transferred to a plain gelatin-coated paper previously treated with a mordanting solution.

A wash-off relief emulsion may be coated either on glass or on celluloid. Glass was used in the Color Snapshots process, nitrate base is used in the Eastman Wash-Off Relief process. An orange dye is used in the latter film to prevent irradiation within the film and to keep the image in the layer nearest the base (exposure is made *through the base*). Any slow bromide emulsion may be used for wash-off relief or imbibition films; but they must contain no hardening agent, and should be dyed with about twenty-five cubic centimeters of 1:200 alcoholic solution of naphthol orange per liter.

Such films may be sensitized with a three per cent solution of potassium dichromate, exposed under a negative through the back, and developed with hot water, then fixed in plain hypo and washed. Or develop in Eastman D-11, rinse well, and bleach for two to four minutes in a mixture of equal parts of:

A. Ammonium bichromate	5	g
Sulphuric acid (conc.)	1	cc
Water	750	cc
B. Sodium chloride	11.5	g
Water	750	cc

Then develop in water at 110° to 125° F., using four or five changes of one minute each, and they are then fixed for one minute in:

Hypo	240	g
Sodium sulphite (dry)	10	g
Sodium bisulphite	25	g
Water to make	1000	cc

Where the dichromatized relief images are stained after being washed out, the three elements in yellow, magenta and blue-green can be assembled to give a three-color transparency. Where the developed, bleached and washed-out images are made, they are used for taking up acid dyes which in turn are transferred to a piece of plain gelatin-coated paper which has been treated with a mordant, as is practised in the well-known Wash-Off Relief process.

Chapter References

1. Charrion and Valette, *Bull. Phot.* 6, 193, 1-10.
2. E. J. Wall, *Photographic Emulsions*, p. 188.
3. T. H. Dixon and Co., Ltd., Letchworth, England.
4. Product of the Atlas Powder Co., U. S. A.

CHAPTER XI

PRINTING-OUT EMULSIONS

Salted Paper — Sensitizing Silk — Printing-out Emulsions — Gelatino-chloride Papers — Collodio-chloride Papers — Self-toning Papers — Silver Phosphate Papers

CERTAIN salts of silver will, if applied to paper, give a visible image on exposure to light under a negative, which is of sufficient density to provide a permanent print. Silver chloride discolors or “prints out” a blue-violet color; organic salts of silver, such as the citrate, oxalate or tartrate, print out a redder color. The organic salts appear to be more sensitive to light when in a humid condition, which explains why so-called print-out papers sensitized with a mixture of the two — as is usually done — yield a redder image if the humidity is high. None of these compounds will give a sufficiently intense image by itself to withstand the fixing bath, and an excess of silver nitrate is required for building-up purposes. The visible image consists of metallic silver in a very fine state of division, and in the heaviest densities there is probably not more than half a milligram of silver metal per square decimeter. The reduced silver is colloidal in character, and some of it is held in solid solution in the excess of silver halide; if, on prolonged exposure, the silver chloride becomes saturated, a deposit of bronze-colored silver metal may then appear on the surface in the deepest shadows.

The simplest possible form of printing-out paper is the old-fashioned “salted paper,” though this is not actually prepared with an *emulsion*. In this process of sensitizing, the original surface of the paper is retained, and photographs printed on it

may be used as the basis for a drawing or for working up with water colors, the silver image itself being removed afterwards. Any good quality drawing paper, such as Whatman's or Rive's, or good unsized writing paper, can be sensitized. It must first be sized or coated with a solution containing the reacting salts:

Water	450	cc
Sodium chloride	15	g
Citric acid	1.5	g
Arrowroot	15	g

The arrowroot is mixed with about fifty cubic centimeters of the (cold) water, and rubbed into a smooth paste. The remaining water with the sodium chloride and citric acid is next added, and the whole is brought to the boil, stirring continually, and boiled for three minutes. When cooling, a skin may form on the surface, and if so, it is removed and thrown away. The solution is then filtered. If a glossier surface is wanted, five grams of gelatin may be substituted for the arrowroot, when of course boiling is not necessary, the gelatin being dissolved with heat and stirring in the usual way.

The salting solution as described can be applied with a wide, soft, camel's-hair or hog's-hair brush, or the paper may be floated upon it a sheet at a time and hung up to dry. It is a good plan to make a mark in pencil on the back of each sheet indicating that the opposite side has to be sensitized. If bubbles form when brushing on to the surface of a rough paper, a little alcohol (three or four per cent) may be used in the solution. The paper must be dried in a room or cupboard absolutely free from dust.

It is best sensitized the night before use by floating it, sheet by sheet, upon the silver bath, which is prepared as below:

A. Silver nitrate	20	g
Water	100	cc
B. Citric acid	15	g
Water	100	cc

A and *B* are mixed, and twenty cubic centimeters of pure grain alcohol added. The solution is used at room temperature, in a perfectly clean dish. A sheet of paper held by the edges is bent into an inverted U, the convex side brought gently into contact with the surface of the sensitizing bath, and the two sides then lowered until the sheet floats upon the liquid. After a minute it is lifted by one corner to see if there are any air bubbles, and if so, these must be removed and the sheet re-lowered on to the solution for a further two minutes. Thick paper may require four to five minutes in all. Rubber gloves should be worn, or the fingers may get badly stained. The sensitized paper is hung up to dry by the corners, in a warm room or dust-free cupboard. All these proceedings can be carried out in Mazda light.

Printing is done in sunlight, and progress may be examined by opening the frame a few feet away from the window. When all details are clearly visible, and the print is appreciably darker than is desired in the final image, the paper is removed from the frame and washed, toned in a gold bath, and fixed. If it is required only as a guide for drawing, it may be simply fixed in twenty per cent hypo, but it will then take on an unpleasant orange color. The *photographic* image after drawing upon it can be removed with Farmer's reducer.

If separate toning is to be given, it is imperative to wash the print beforehand until all free silver nitrate has been removed; this will be apparent when the wash-water no longer becomes milky through the formation of silver chloride. A good toning bath is as follows:

Gold chloride	0.1 g
Sodium acetate	2.8 g
Water	400 cc

When the print has acquired a purple tone, it is rinsed and

fixed for five minutes in a ten per cent hypo solution, and is finally well washed. By the use of a combined toning and fixing bath the print can be put without washing into the solution, toned and fixed simultaneously, and then finally rinsed. Such a bath may be made up thus:

Water	300	cc
Hypo	100	g
Lead acetate	0.3	g
Gold chloride	0.15	g
Powdered chalk	7.5	g

Shake up well, stand overnight, and decant the clear solution for use.

SENSITIZING SILKS AND FABRICS. — For printing photographs upon silk or other fabric, sensitizing is best done with the substitution of Iceland moss for arrowroot, starch, or gelatin. This is a dried seaweed collected on Atlantic coasts, and is made into an "infusion" by mixing 2.5 g of the moss with 500 cc of boiling water. It is decanted and filtered, and when cold is of a syrupy consistency. To it is added:

Sodium chloride	20	g
Glacial acetic acid	50	cc

The mixed solution is used in a dish, and the pieces of material are gently lowered on to the surface, the object being to coat the surface of the material only, and to prevent as far as possible the solution from penetrating through to the back. After two minutes' flotation, the pieces of silk, etc., are lifted by two corners and hung up to dry on a stretched cord, and left until they no longer smell of acetic acid. They are then sensitized by floating on:

Silver nitrate	25	g
Citric acid	20	g
Grain alcohol	20	cc
Water to make	250	cc

A high-contrast negative should be used for printing (γ 2 to 2.5), and the image printed deeply and then treated with a combined toning and fixing bath. Wash and dry and smooth out cautiously with a moderately hot iron.

Plain salted paper as above described was followed by a much more stable product, prepared with a coating of salted albumen and sensitized afterwards with silver nitrate, which held the field for many years. After this era of albumenized paper came the far more practical gelatino-chloride paper popularly known as printing-out paper in America, and as P.O.P. in England. This was baryta paper coated with a single emulsion of silver chloride in gelatin, containing a large excess of silver nitrate, and it had both before and after use comparatively high keeping qualities. It printed rapidly, gave a superb range of tone, and could be toned with gold, platinum or palladium, giving an image which would last for ten years or more.

The need for an excess of silver nitrate makes it necessary to select paper of great purity for coating gelatino-chloride emulsions, and fairly heavily baryta-coated rag paper has been used. After printing-out in daylight, the excess of free nitrate is removed by washing, and the prints are then toned and fixed. To avoid the trouble of toning, a soluble gold salt such as the thiocyanate was incorporated in the emulsion itself, making self-toning papers which acquired a gold purple tone during fixation.

One form of print-out emulsion giving brilliant prints but of only moderate keeping quality is made as follows:

A. Water	750	cc
Ammonium chloride	2.5	g
Sodium potassium tartrate	5	g
Gelatin	80	g
B. Silver nitrate	25	g
Citric acid	10	g
Water	250	cc

Solution *B* is added to *A* in a slow stream while the crock is kept stirred, both solutions being at 105° F. (40° C.). The mixed emulsion is almost transparent at first, but soon becomes turbid. After about ten minutes, forty to fifty cubic centimeters of denatured spirit is added, and slowly, with stirring, twenty cubic centimeters of a 2.5 per cent solution of chrome alum. The emulsion is filtered through felt, or two thicknesses of linen, and coated at once. It cannot be set off and remelted. Increase in the amount of citric acid tends to give higher contrast; substitution of an equivalent amount of ammonium citrate for the Rochelle salts (sodium potassium tartrate) tends to give fuller half-tones. The addition of ten cubic centimeters of a twenty-five per cent solution of stronger ammonia water will give increased sensitivity and somewhat bluer tones. When ammonia is used, however, the emulsion should be stood after its addition for half an hour at 105° to 110° F. before coating. To mat the emulsion, fifty grams of rice starch, ground to a paste with a little water, is added before filtering. The mat emulsion is best coated on *glossy baryta* paper.

Another reliable formula for a printing-out emulsion is the following:

A. Gelatin	24	g
Ammonium chloride	0.8	g
Water	200	cc
B. Tartaric acid	0.8	g
Sodium bicarbonate	0.4	g
Potash alum	0.5	g
Water	30	cc
C. Silver nitrate	10	g
Citric acid	2	g
Water	45	cc

A and *B* are heated to 110° F. and mixed; solution *C* is then added slowly with stirring, at the same temperature. Final ad-

ditions are twenty cubic centimeters of grain alcohol and five cubic centimeters of 2.5 per cent chrome alum solution.

It has been suggested that the decomposition of the gelatin by free silver nitrate can be obviated by the use of a sufficient amount of organic salt, such as ammonium or potassium citrate, to take up the excess of silver nitrate over the combining weight of chloride. Thus for 100 grams of AgNO_3 , 18.3 grams of sodium chloride and 29 grams of potassium citrate would be used, keeping the citric acid at about sixty per cent of the silver.

The use of collodion in place of gelatin offers some attraction, and collodio-chloride printing-out papers have enjoyed considerable popularity. The drawback to the use of collodion in laboratory experimentation is its very high inflammability. The solvents used are not only inflammable to a marked degree, but when diluted with air may form highly explosive mixtures. In factory practice not only can fire risks be eliminated by suitable precautions, but methods are adopted of recovering the solvents for use again.

A formula which may be made up successfully in small quantity is given below:

A. Pyroxylin or "celloidin"	10	g
Ether (methylated)	200	cc
Alcohol	200	cc
Castor oil	2	cc
B. Lithium chloride	1.2	g
Strontium chloride	1.2	g
Alcohol	35	cc
C. Silver nitrate	10	g
Distilled water	10	cc
Alcohol	25	cc
D. Citric acid	2.5	g
Alcohol	35	cc

Mix *C* and *D*, and add gradually to the collodion *A* in a large

flask, with constant agitation. Then add *B* very gradually, with constant shaking. Lastly add 2.5 cc glycerin. Stand for twenty-four hours before coating on baryta paper.

An alternative formula ¹ runs as follows:

A. 4 per cent collodion	500 cc
B. Alcohol	50 cc
10 per cent aqueous solution of strontium chloride	3 cc
10 per cent aqueous solution of lithium chloride	1 cc
C. 50 per cent solution of silver nitrate	24 cc
Alcohol	50 cc
D. 25 per cent aqueous solution of citric acid ..	60 cc
Alcohol	25 cc

A and *B* are thoroughly mixed at room temperature, a two-liter Pyrex flask being very convenient. *C* and *D* are then mixed together and added to the mixture in the flask, ten to fifteen cubic centimeters at a time, with vigorous shaking. When emulsification is completed, the following finals are added:

50 per cent castor oil in alcohol	3 cc
Alcohol	25 cc
50 per cent glycerin in alcohol	8 cc

This emulsion can be made self-toning by adding 0.15 grams of gold chloride dissolved in ten cubic centimeters of alcohol; the addition of ammonium thiocyanate or lead acetate or nitrate has also been suggested. Self-toning emulsions are usually unstable and should be coated at once.

The coating of collodion emulsions for experimental purposes is by no means easy. Baryta paper *can* be unrolled on the emulsion placed in a dish, as has been described elsewhere (p. 163), but the film may form in tiny wrinkles and give a broken surface. Small pieces can be coated individually by

turning up the edges about a quarter-inch all around, laying the sheet on glass, and coating as a glass plate. If an excess is poured on, and after setting for a few moments is poured *off*, the paper may be held at one corner and given a zigzag movement to prevent wrinkling. The warning against the high inflammability of collodion and its solvents, especially when used in open dishes or during evaporating when drying the paper, must again be emphasized. Positively no naked lights may be used, no smoking, and no use of electric heaters having bare resistance elements. The room should be kept cool, and should be well ventilated.

Stripping-collodion may be made by first coating baryta paper with an eight per cent gelatin solution, then with the collodion emulsion. The gelatin coat is, of course, first dried. After the print has been toned and fixed, immersion in warm water will soften the gelatin, and the collodion image can be floated off.

While printing-out papers have gone out of fashion on account of the convenience of development papers and their greater working rapidity, they are capable of giving exceedingly beautiful results, and there is some indication of their re-introduction. The experimenter in emulsion work will certainly find a great deal of fascination in the printing-out field, and ample scope for investigation.

SILVER PHOSPHATE SENSITIZERS. — Phosphate of silver is formed by the reaction of sodium phosphate, Na_2HPO_4 , or tri-basic sodium phosphate, Na_3PO_4 , with silver nitrate. It is more sensitive than the chloride, and must therefore be dealt with in yellow light. It gives a somewhat exaggerated latitude, so that it is best suited to hard, vigorous negatives. A precipitate of silver phosphate dissolved in an organic acid, such as citric acid, can be applied with a brush to raw paper, or the salt itself may be precipitated in collodion as suggested by Valenta.² Here 2.9

cubic centimeters of phosphoric acid of specific gravity 1.265 was added to 200 cubic centimeters of collodion, together with 7 grams of citric acid previously dissolved in 14 cubic centimeters of alcohol. This was then mixed with:

Silver nitrate	10	g
Water	125	cc
Alcohol	20	cc
When dissolved, add Lithium carbonate	7.5	g

When the evolution of carbonic acid has ceased, 1.5 cubic centimeters each of glycerin and grain alcohol are added.

Silver phosphate images may be developed with a weak solution of metol acidified with acetic or tartaric acid.

Chapter References

1. A. Truum, Die Herstellung photographischer Papiere, p. 300.
2. E. Valenta, *Phot. Korr.*, 37, pp. 313, 419, 1900.

CHAPTER XII

TESTING EMULSIONED PRODUCTS

Testing Equipment — Estimation of Speed and Quality — Interpretation of the Characteristic Curve — Measurement of Color-sensitivity — Photometers and Density Meters — Keeping Tests

AN important part of the routine of sensitive material manufacture lies in the adequate testing of the finished products. In any form of investigation, exhaustive tests of the coated plates, films or papers will be more productive of results than the making of numbers of more or less random experiments. Some form of sensitometric test is required, and the character of different emulsions must be deduced and compared. Sensitometric work demands suitable apparatus, which may be somewhat costly, but it must be regarded as absolutely indispensable and a very sound investment where commercial work is envisaged. Where the products are being made for experimental purposes, and do not have to compete with other manufactured articles, a great deal can be accomplished with the aid of more modest equipment.

The main characteristics of plates, films, and papers are most simply represented by the type of curve originated by Hurter and Driffield, which shows the relationship between the photographic response of any individual material after development and the exposure to light required to produce it. As we have seen, emulsions are, in general, sensitive not only to visible light of 400 to 700 $m\mu$, but to radiations of shorter wavelength, especially the ultra-violet, X-rays and the radiations emitted by radioactive bodies. A developable effect is also produced by a static discharge in contact with the film, and to some extent

by pressure. Bloch states¹ that pressure or abrasion marks render the emulsion *insensitive* to subsequent light action.

The developed image consists of reduced metallic silver grains, and the mass of reduced silver per unit area is proportional to the logarithm of the opacity. Opacity is the ratio of the incident to the transmitted light, or the reciprocal of transmission, $\frac{I}{T}$. The need for expressing it logarithmically can be seen from

the simple table showing that the quantity of light transmitted by an increasing number of layers of an absorbing material each one of which absorbs *half* the incident light, proceeds geometrically and not arithmetically, as under:

	<i>Proportion of light transmitted</i>	<i>Opacity</i>
1 layer	$\frac{1}{2}$	2
2 layers	$\frac{1}{2}$ of $\frac{1}{2} = \frac{1}{4}$	4
3 layers	$\frac{1}{2}$ of $\frac{1}{4} = \frac{1}{8}$	8
4 layers	$\frac{1}{2}$ of $\frac{1}{8} = \frac{1}{16}$	16
5 layers	$\frac{1}{2}$ of $\frac{1}{16} = \frac{1}{32}$	32

and so on. Expressed as logarithms to base 10, we have (approximately):

log (opacity) 2	= 0.3	(2 = 10 ^{0.3})
log 4	= 0.6	(4 = 10 ^{0.6})
log 8	= 0.9	(8 = 10 ^{0.9})
log 16	= 1.2	(16 = 10 ^{1.2})
log 32	= 1.5	(32 = 10 ^{1.5})

and so on.

The logarithm to base 10 of the opacity is termed the density. The density of the coated film bears a constant relation to the logarithm of the exposure over a range of illumination $I \times T$ which is dependent on the particular emulsion. The curve connecting density with *log* opacity, usually referred to as the H

and D curve after Hurter and Driffield, or the characteristic curve, takes the general form shown in Fig. 59. It will be seen

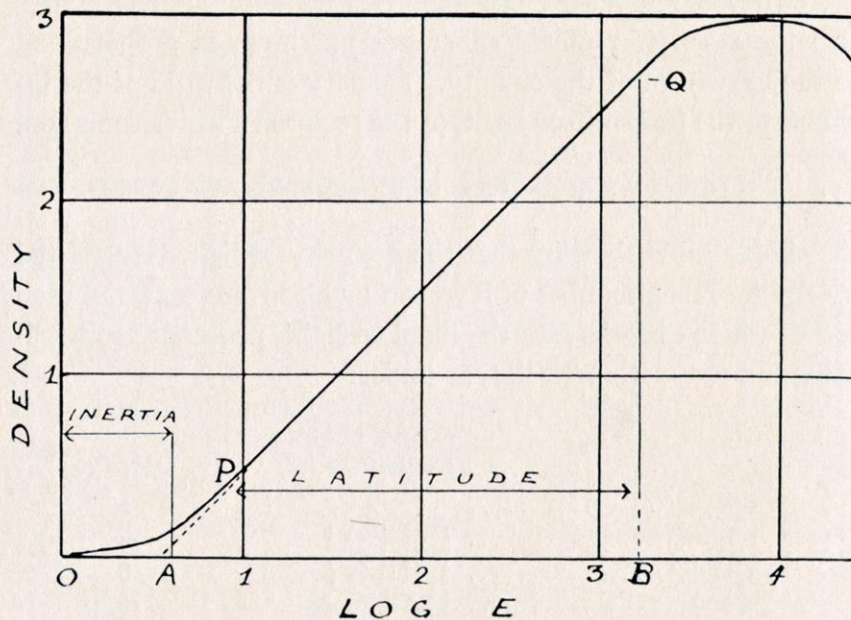


FIG. 59

that the increase in density for increase in *log* exposure is not equal for the lower exposures, but is progressively greater as exposure rises, and that the shape of the curve is curved in these lower densities, known as the foot or toe. After exposure has exceeded a certain amount, however, density increases by regular amounts over a *period of correct exposure* represented by the straight-line portion *PQ*, this part of the curve giving us a measure of the *latitude* of the emulsion. On very considerable exposure, the curve is seen to turn over, when still further increases in exposure (*overexposure*) actually produce less density instead of greater. This is the region of solarization or *reversal*, and is usually encountered at an earlier stage in the

case of fast large-grained emulsions than it is in slower, more fine-grained emulsions.

The characteristic curve gives us an immense amount of useful information, enabling us to make a very complete post-mortem of an experimental emulsion, or the effects on its quality of any variations which may have been made in the course of experiment. It will be seen in Fig. 59 that on extending the straight-line portion to cut the *log* exposure axis, it cuts it at a point, *A*. The length *OA* represents the *inertia* of the material, and this is inversely proportional to the so-called *speed*. It must be emphasized, however, that the characteristics exhibited by any such H and D curve, and the inertia and speed deduced therefrom depend upon the particular developer used, on the time of development and its temperature, and — to some extent — on the spectral quality of the light used in exposure.

If *log* exposure is spaced along the horizontal axis equally with density along the vertical, so that for example *log* exposure of 3 measures the same as density 3 on the graph, then we obtain a universally recognized means of measuring contrast or gamma, γ . If the straight-line portion of the curve be at an angle of 45° with the *log* E axis, then $\text{gamma} = \tan 45^\circ$, or 1. Generally, $\gamma = \tan \theta$, where θ is the angle made by the straight-line part of the curve with the *log* E axis.

As contrast depends on the amount of development, and inasmuch as the rate of development depends on the temperature of the solution, it is usual practice to publish Time/Temperature/Gamma curves. An exhaustive series of these will be found in Morgan and Lester's "Photo Lab. Index," measured for practically all marketed materials. Such curves are also being extensively published by manufacturers, and their preparation and issue with new sensitized materials should be regarded by new entrants into the manufacturing field as in-

dispensable. An example of the form in which sensitometric data is supplied is seen in Fig. 60, reproduced from "Kodak Films."

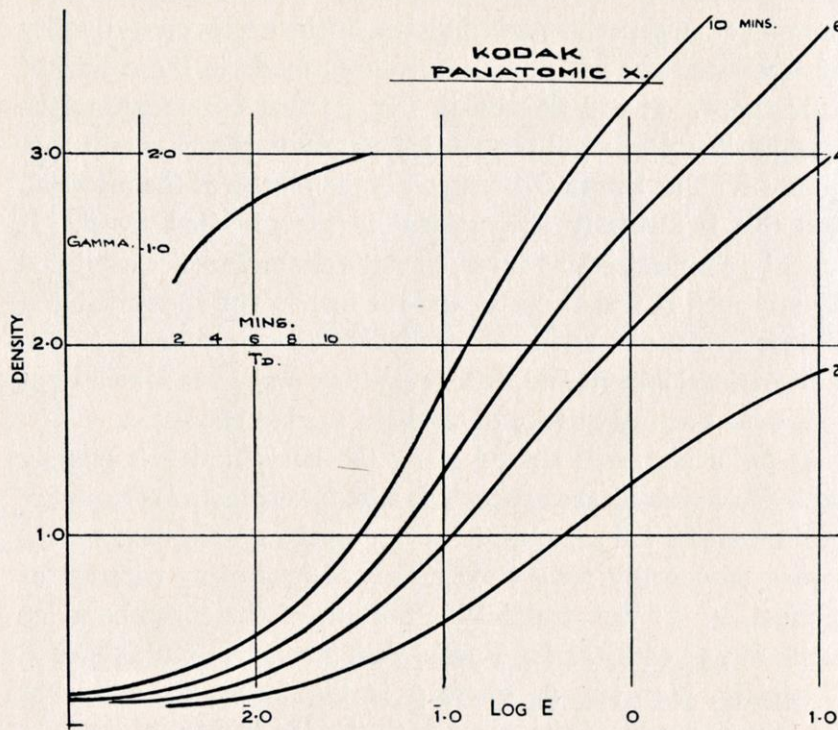


FIG. 60

In Fig. 61 we see a number of curves plotted for one material, developed for increasing times. The contrast is low at short development, rising with increasing time of development until the top curve is reached after a gradual falling off of the rise with time. In this case after eleven minutes at 70° F., longer development fails to increase contrast. In other words, *gamma infinity* has been reached, denoted by γ_{∞} . While, therefore, gamma is a measure depending on a particular developing solu-

tion, its temperature, and the time of development, gamma is a concrete factor which gives a definite idea of the ultimate performance of an emulsion. Gamma infinity is largely independent of the wavelength of the light used in exposure if the

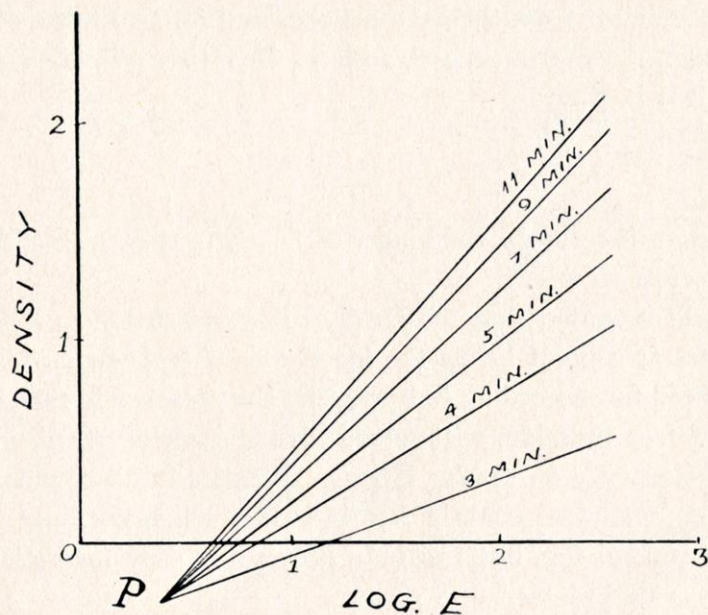


FIG. 61

plate be developed to gamma infinity², whereas a color-sensitive emulsion *not* developed to γ_{∞} is definitely dependent on wavelength.* It is for this reason that the yellow printer negative in one-shot camera work (exposed through the blue-violet filter) is generally given a time of development increased from twenty-five to one hundred per cent over the times allotted to

* Certain recently introduced emulsions of the panchromatic type are claimed to give a consistent gamma throughout the spectrum, and the yellow, red, and cyan printers can thus be all given the same time of development.

the red and cyan printers. In cases where narrow-cut filters are used in separation work from color transparencies, the time of development should actually be varied for each of the three. Gamma infinity being an important factor from an emulsion-making point of view, the following simple formula for deducing it from the gammas obtained for two times of development, γ_1 for a time T , and γ_2 for a time $2T$, one double the other, is given:

$$\gamma_{\infty} = \frac{\gamma_1^2}{(2\gamma_1 - \gamma_2)}$$

In using this formula, the higher of the two gammas should not be too close to γ_{∞} .

It will be noted that the family of curves shown in Fig. 60 all meet at a point below the $\log E$ axis if extended. This is accounted for, according to Nietz,³ by the presence in the emulsion of free bromide, without which the meeting point would be substantially on the $\log E$ axis. Practically all commercial bromide emulsions contain free bromide, which not only minimizes general fog, but assists in preventing edge formation of fog on coated plates.

It has been stated⁴ that "the method devised by Hurter and Driffield in 1890 for studying the properties of a photographic emulsion has been extremely fruitful and still furnishes the most complete information on the different properties of sensitive emulsions, and represents them graphically under the most favorable conditions. At the same time the mode of numerical expression of sensitivity proposed by them, (H and D speed) has now scarcely any significance. At the time of Hurter and Driffield, already long past, the different types of emulsions all had characteristic curves of the same general form, and in order to express the relative sensitivity of two plates it was sufficient to measure (parallel to the exposure axis) the distance between

the corresponding curves after the two plates had been developed to the same gamma. Since 1910, however, new types of emulsions have appeared with characteristics very different from these old emulsions, and it is impossible to imagine a single numerical value which defines at the same time the form of a curve and its position relative to another one."

A simple example of the position can be seen in Fig. 62. This

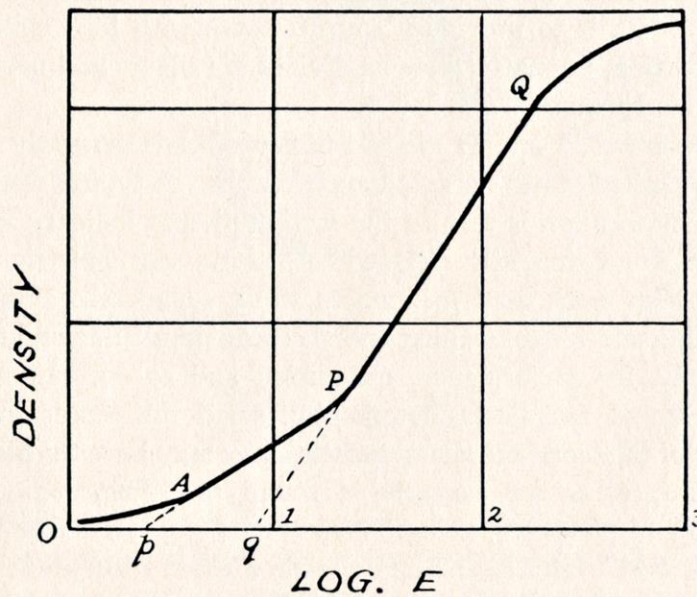


FIG. 62

is a curve representative of many super-speed emulsions. It may be considered as having two straight-line portions, the earlier of them really a prolonged foot. If we extend the foot portion, AP , to meet the $\log E$ axis, it gives an inertia of Op ; whereas if we extend the straight-line portion, PQ , it meets the $\log E$ axis at q , giving an inertia of Oq . The speed of the emulsion, obtained by dividing Op into a constant as would be done in H and D practice, is obviously far greater than the

speed measured by dividing Oq into the same constant. Yet the studio portraitist may do all his work with low densities on the foot portion and find the material extremely fast, while the man who wants heavier densities must use the PQ part of the curve, and will find the emulsion quite moderate in speed. This case is typical of mixed emulsions, and can occur to a very appreciable extent in the case of split silvers, where one silver is re-dissolved and the other added plain, etc. The emulsion-maker's art is to provide a smooth curve with long straight-line portion, no matter how he divides his silvers and manipulates his ripening.

The broad H and D method is nevertheless generally used in the United States for sensitometric work. A typical example of its application is seen in the motion-picture industry where a staff is continuously engaged in making sensitometric tests of all film stock used for camera work, sound recording and printing, and for controlling and checking developing and other solutions for performance, exhaustion and so on. In many branches of technical photography, small differences in the shape of the toe of the characteristic curve may have the highest significance, as for example in sound recording, radio facsimile and photo-engraving. Needless to say, refined sensitometric work of this type is not possible without adequate laboratory plant and physical apparatus, and more particularly in the absence of machine-coated materials.

In experimental work with emulsions, a great deal of useful information can be obtained as to the effects of variations in treatment, modifications in formula, and so on, with a good step-wedge, a stable light source, temperature-controlled development, and some dependable form of densitometer. The step-wedge provides us with an intensity scale of exposure, as against the time scale of the Hurter and Driffield or Scheiner sector wheels. The usual sector wheel of Hurter and Driffield

has nine slots (Fig. 63), each one subtending double the angle of the previous one, thus giving an exposure range of 1:256, the ratio being $\times 2$ for each step. The disc W (Fig. 64) is mounted



FIG. 63

vertically on a shaft driven by motor. A plateholder *P*, behind the upper half of the disc, receives light through the slots as the disc is rotated by a driving wheel, *D*. A controlled light source, *L*, filtered to daylight and thoroughly screened, is placed at a fixed distance—usually one meter—from the sector wheel, which may be turned rapidly (when the intermittency effect creeps in), or through one complete turn for the entire exposure. The lamp, *L*, which must be housed in a dead-black box with suitable aperture facing the sector wheel of say one inch square, is run from a storage battery *B*, through a resistance *R*, with regulating contact *K*. An accurate voltmeter such as a Weston meter sensitive to within ± 0.2 per

cent, is shunted across the lamp terminals, and the resistance is set to give, say, 5.8 volts with a 6-volt lamp. This slight under-running tends to give uniformity and to increase the useful life of the lamp. Hurter and Driffield used a "standard candle" as their light source; Eder subsequently adopted a small benzene lamp; Sheppard and Mees employed an acetylene flame burning under constant pressure. Today secondary standards are most conveniently obtained with incandescent lamps, but it must be understood that photographic sensitiveness varies quite considerably with the spectral quality of the

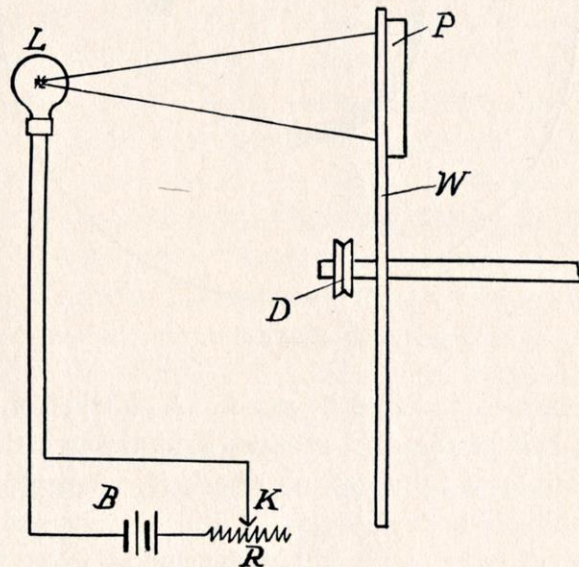


FIG. 64

light used, so that this must be correctly defined and properly controlled. The spectral energy distribution of incandescent lamps varies greatly with filament temperature, which in turn varies with applied voltage.

Probably the most useful type of step-wedge is one having

twelve steps — *no* density at the first ($d = 0$), complete opacity at the twelfth ($d = \infty$), and ten intermediate steps of:

Density 0.3	having approximately transmission	1/2
0.6		1/4
0.9		1/8
1.2		1/16
1.5		1/32
1.8		1/64
2.1		1/128
2.4		1/256
2.7		1/512
3.0		1/1024

The Eastman Kodak Company supplies wedges having twenty-one steps with densities ranging from 0.15 to 3.0, the step increments being 0.15 instead of 0.3, the opacity ratio of successive steps being thus $\times \sqrt{2}$ instead of $\times 2$. The Ilford Company, Ilford, London, England, specializes in step-wedges, making them to any reasonable specification. A four by five inch step-wedge with ten steps costs fifteen to twenty dollars. Alternatively, by obtaining some neutral gray gelatin of three or four densities, a step-wedge can be built up on a piece of glass, using different combinations for the successive steps. Eight strips one-half inch deep and four inches wide can be mounted on a 4 by 5-inch glass, leaving the top half inch clear to give total transmission and blocking out the last half inch with a strip of dead black paper to give total opacity.

The wedge must be used in a solid plateholder or frame of ample dimensions, as shown in Fig. 65, which can be placed on the bench at a measured distance from a suitable and controllable light source, such as a 6 or 8-volt motor headlamp run from a storage battery with a potentiometer at a voltage preferably of rather less than six volts. A tungsten-to-daylight filter such as the Wratten 78 will filter the light and give results more closely approximating practical daylight use.

Sensitometry connected with emulsion-making experiments is not quite on a par with the general testing of photographic materials, as in most cases comparisons of speed and characteristics of members of a series of similar emulsions are the chief

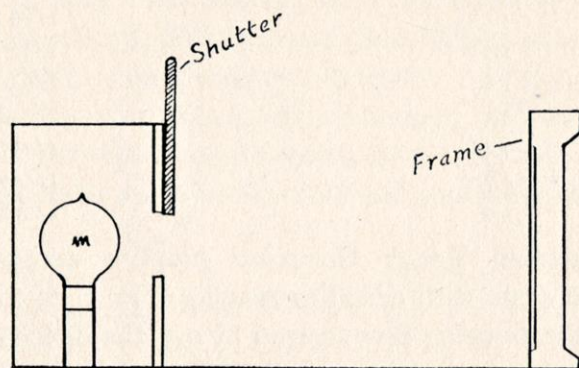


FIG. 65

concern. Relative speeds can be obtained by means of the points on the $\log E$ axis at which the straight-line portions of the curves, when prolonged, intersect it. The antilog of the difference between the $\log E$ readings will give the speed ratio. Contrast can be estimated by measuring the slope of the straight-line portion of tests developed to gamma infinity, and the materials can then be classified for general reference into groups such as:

Flat	when γ_{∞} is less than 1.2
Normal	when γ_{∞} lies between 1.2 and 1.6
Medium	when γ_{∞} is greater than 2.0
Contrasty	when γ_{∞} is above 2.7
Hard	when γ_{∞} lies between 3.5 and 4.0
Extremely hard	when γ_{∞} lies between 4.0 and 5.0

Such comparisons may be made with any stable light source, and the necessary exposure to give a reasonably straight-line portion of the curve. If, on the other hand, densities be plotted

against exposures measured in lumens per square meter \times seconds, or measured from a light source of known candle power of geometrically decreasing strength as obtained with a wedge, comparative speed determinations can be made with considerable accuracy. The step-wedge which can be used in a plateholder at a fixed distance from a standard light source, which distance can be varied with slow or extreme speed emulsions, is probably the best for experimental work, while an accurately cut sector-wheel with a satisfactory secondary standard light source is more generally useful in works laboratories.

In view of the very high humidity experienced in many parts of the country, and the utterly inadequate means of dealing with it which are found in most amateur laboratories, attention should be drawn to the effect which humidity may have on sensitometric tests. The importance of this effect was emphasized by Renwick,⁵ in connection with the testing of negative and positive motion-picture film stock. A simple method of partial control in use by the author may be recommended. This is to place the samples of sensitive material to be tested in a large desiccator for forty-eight hours before they are required, using a saturated solution of sodium chloride (kitchen salt) in the bottom. This maintains an "atmosphere" of about seventy-five per cent relative humidity, which is more or less representative of average conditions in summer time in the United States. It was found by Dimitroff⁶ that the background density in many cases increases with decrease of humidity, and that in some cases the graininess of an emulsion appears lessened if the plate is treated with dry air.

The control of development is of prime importance. It has been pointed out that the characteristic curve depends upon the particular developing formula used, so that the need for a standard solution, used at a definite temperature, is self-evident.

The old pyrogallol-soda formula recommended for a long time for H and D determinations, should be replaced by such a formula as D-11, D-72 or one of the fine-grained type, although a developer *without bromide* is desirable for investigation work. If a number of comparative sensitometric tests be made, it is important that they all be made together for the same time and with as nearly as possible the same amount of agitation. For such a purpose the use of a Dewar vertical vacuum flask may be recommended, where three or four strips can be attached by rubber bands to the sides of a triangular or rectangular stick of wood and immersed in the temperature-controlled solution.

To recapitulate, the emulsion chemist should use, for each family of tests,

- (a) a constant developing solution, freshly made.
- (b) a constant time of development.
- (c) a constant temperature.

Where a gamma/time curve is required, conditions (a) and (c) must be enforced, the time alone varying, with a short-stop bath used between development and fixing or the immediate transference of the test from developer to a strong acid fixing bath. A vertical developing tank standing in an outer bath of water is recommended for gamma/time work, the tests being suspended vertically in dilute developing solution, giving of course proportionally longer time. The liberation of halogen in the process of reduction of the silver bromide during development and its conversion by the accelerator into alkali bromide, will restrain development in adjacent strips and give erroneous or streaky densities unless proper agitation is applied. Developing sensitometric tests in a flat dish and removing the by-products of development by gentle brushing with a soft camel's-hair brush, has been recommended. Agitation of the plate or film, however, increases the rate of development, so that means must be adopted of giving an average amount of agitation to

each batch of tests. Much valuable information on the effects of agitation has been published in Eastman Kodak research communications.

Densities can be measured directly by means of their absorption of a beam of light as recorded by a photo-electric cell. Articles describing the construction of *densitometers* of this

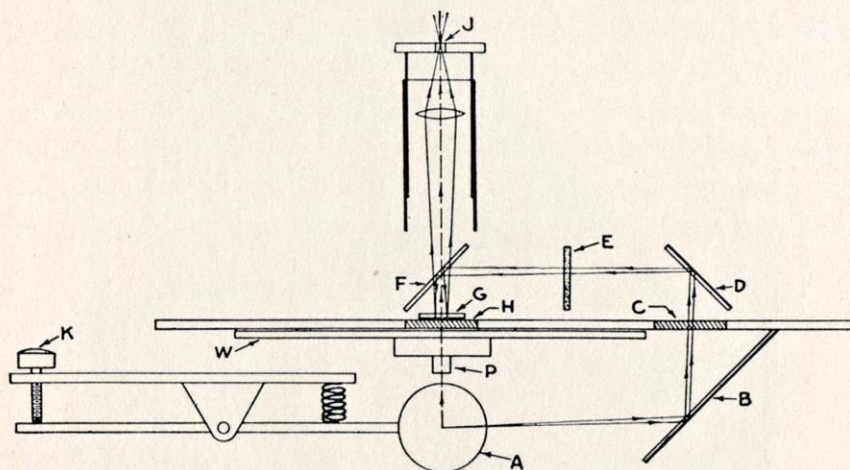


FIG. 66. DIAGRAM OF CAPSTAFF DENSITOMETER OPTICAL SYSTEM

type have appeared many times in recent photographic literature. Two beams of light may be compared in another type of instrument, one passing straight through the density to be measured, the other being extinguished by suitable means until it matches it. Such instruments depend on the use of crossed Nicol prisms, or on the use of a graduated gray wedge. The Hüfner spectro-photometer and the Hilger-Nutting spectro-photometer are examples of the first-named, while the density meter worked out by the British Photographic Research Association depends upon matching the direct and the wedge-extinguished beams by means of a photo-cell.

Another type of densitometer throws the two beams from the



FIG. 67. CAPSTAFF DENSITOMETER

density patch and the gray wedge into an eyepiece, the wedge being brought to a position where it equalizes them visually. The position of the sliding or revolving wedge is read off on a calibrated scale in densities direct. An instrument of this type, due to Capstaff and Purdy,⁷ is manufactured by the Eastman Kodak Company; a more elaborate model is made with which reflection densities as well as transmission densities can

be measured. The Capstaff instrument measures silver deposits from a density of 0 to 3.0, and will deal with areas of only one-half square millimeter, being particularly designed for use in the motion picture industry. The optical system is seen in Fig. 66.

Light from source *A* illuminates at *H* the density to be measured, and furnishes the comparison beam. A photometric field at *G* is obtained by the aid of mirrors *B*, *D*, *F*, and *G*. *W* is a circular wedge, shown in Fig. 68, for decreasing by a known amount the intensity of the light illuminating the density. *J* is an eyepiece for viewing the field, in which the density is seen as a central spot in a circle of variable density; when the two beams are matched, the central spot vanishes. The combined

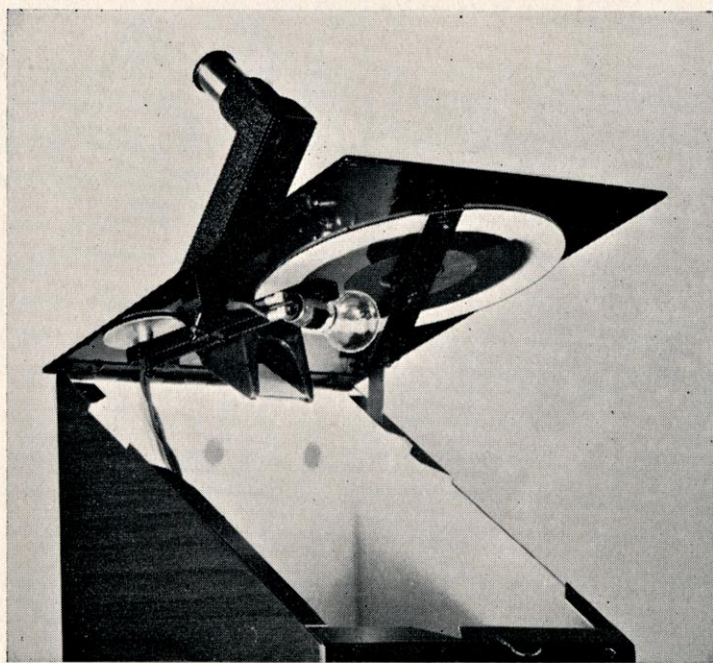


FIG. 68. DENSITOMETER HEAD RAISED SHOWING CIRCULAR WEDGE

densitometer for measuring negative or print reflection densities is seen in Fig. 67.

In connection with density measurements, it must be borne in mind that the reduced silver grains scatter the light to an extent depending on the emulsion characteristics, and that a density reading obtained by a beam of parallel rays will differ from that obtained by diffuse light. Diffuse density meters have a small opal or finely ground glass directly under the plate or film so that the light is completely scattered. The ratio of density (parallel) to density (diffuse) can yield valuable information as to the physical quality of the developed emulsion.

A simple and inexpensive wedge densitometer designed by Sanger Shepherd and improved by W. B. Ferguson⁸ is shown in Fig. 69. Light falls directly on the front of the inclined in-

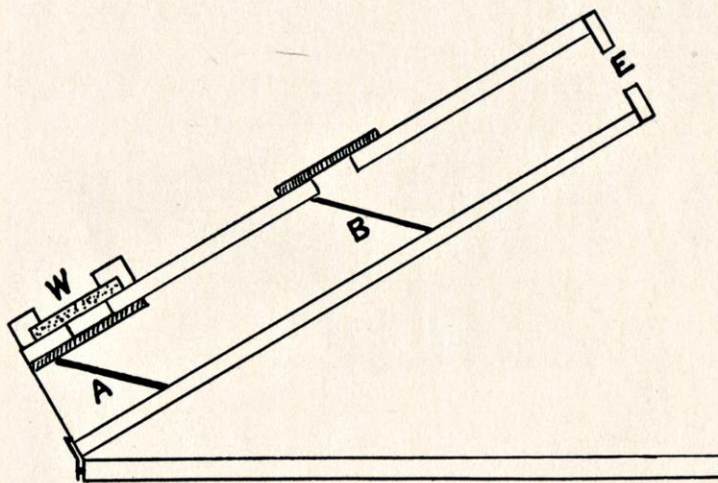


FIG. 69

strument, as from a north window. One beam of light passes through the calibrated gray wedge, *W*, and is reflected into the eyepiece, *E*, by the mirror *A*. The other beam passes through the density patch to be read (laid over the middle aperture), and is reflected by the mirror, *B*, so as to appear in the eyepiece

contiguous to the first beam. Both beams are scattered by opal glass. The wedge, *W*, is slid along until the two beams appear of equal brightness. Readings can be obtained with an accuracy of about \pm two per cent.

A simple photo-electric densitometer devised by Schoen is seen in Fig. 70. *E* is a lamp run at controlled voltage by means

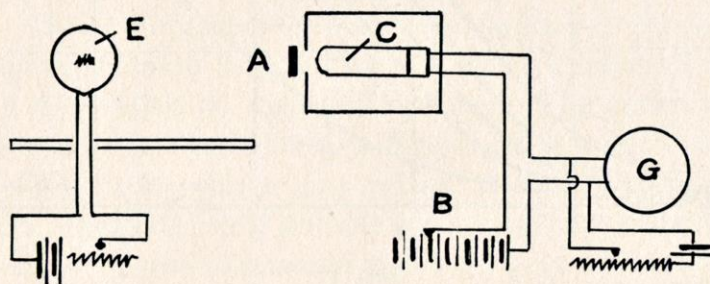


FIG. 70

of a potentiometer. *A* is a slot over which the density patch is placed. *C* is a thalofide cell (Case) coupled up with a galvanometer and battery, *B*. The galvanometer, *G*, is brought to the null point with the shunt circuit shown, and the density then introduced at *A* and measured by means of a previously calibrated dial or by a table prepared from known density measurements, or by interpolation on a prepared curve.

If an emulsion be exposed through a small circular hole placed in contact with the film, for increasing times of exposure, the diameter will spread as exposure is increased, and the slope of a curve connecting diameter with exposure was termed by Goldberg the turbidity factor; this was found to be zero in the case of Lippmann plates (p. 135), although no absolute relation between the factor and the grain of a plate was established. The *sharpness factor* of an emulsion has been given by Goldberg as

$$\frac{\text{gamma}}{\text{turbidity factor}}$$

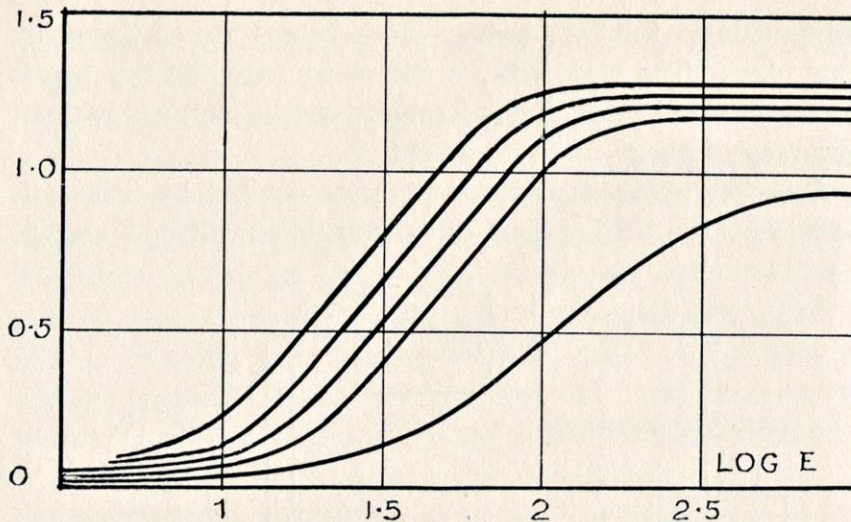


FIG. 71

Translated into practical language, an emulsion to give sharp images should have a high development factor (gamma) and low turbidity, a long straight-line portion to its characteristic curve, and should rise to the maximum slope at as low a density as possible, i.e., not have a long, rounded toe.

So far, we have been dealing with measurements of transparent images only, such as negatives or transparencies, on glass or celluloid. When, however, we come to deal with development papers, we must make measurements of the light reflected from the *surface* of the image. The contrast as seen by reflection increases rapidly at first, and then becomes stationary, all the deeper tones being lost or merged in papers having too high a contrast when fully developed out. This is seen from the characteristic curves given by Mees (Fig. 71), for a bromide paper. It will be noticed that the latitude and gamma remain fairly constant over most of the range, due largely to a considerable regression of inertia with increasing time of development, indicating that good prints can be obtained of varying contrast

by a well-coordinated variation of development time and exposure.

For sensitometric tests of development papers, a reflection densitometer is needed, and probably no more convenient one exists than the Eastman Kodak meter already referred to, of Capstaff and Purdy. An excellent densitometer is made, however, by W. Watson and Sons, Ltd., of High Barnet, Herts, England. This is the outcome of many years' work with the original selenium instrument designed for the British Photographic Research Association by Toy and Rawling.⁹ The design of the negative density meter is seen in Fig. 72. *C* is a photo-electric cell, and *W* is the neutral gray wedge. A carrier, *E*, holds the cell and is provided with suitable adjustments for bringing two windows into correct alignment in relation to two diffusing opals O_1 and O_2 . The wedge is held in a U-shaped bracket which is

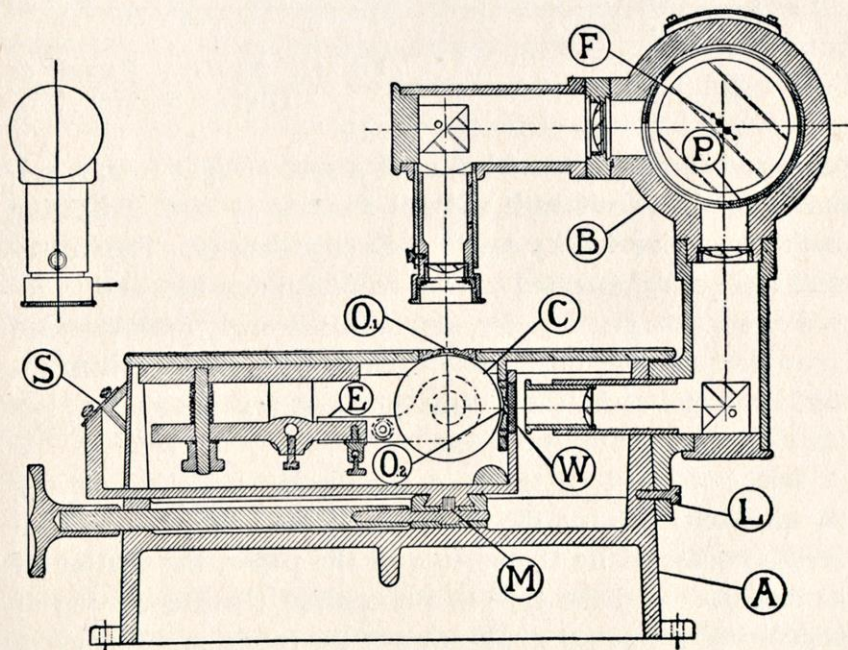


FIG. 72

fixed to a slide provided with a rack, M , by means of which the wedge can be moved across the light beam. The other end of the bracket carries a vernier which moves on the scale S . A single light source, F , is used. The light beam is alternately directed by means of a lever on to the cell through the density

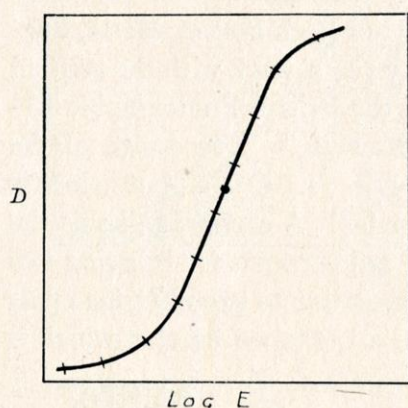


FIG. 73

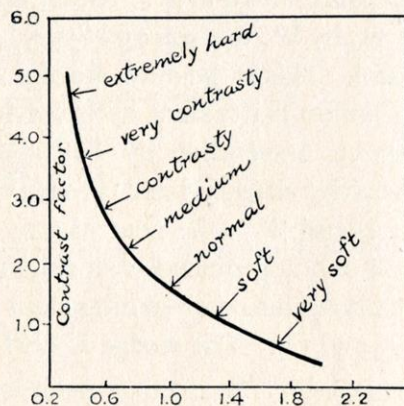


FIG. 74. NEGATIVE RANGES OF CONTACT PRINTS

patch and through the wedge, until a spot of light from a galvanometer in circuit with the cell remains at zero, indicating that the negative density equals the wedge density. The instrument has been elaborated to read reflection densities and to record directly on graph paper, and can be strongly recommended for works practice. The cost of the density meter, galvanometer, lamp and scale, single-tube amplifier and automatic plotting device is, in England, \$625.

Some care must be taken in considering reflection density measurements because the character of the image can be considerably affected by the surface of the paper, the coating of the emulsion, and the type of pre-coating (baryta coating or sizing) used before the application of the emulsion. The effect of the non-stress coating should be negligible. The coating

weight can also affect the differentiation of the heavy densities, which are easily lost by too much silver. In dealing with any serious sensitometric work on development papers, the reader is particularly referred to the papers of L. A. Jones on paper contrast,¹⁰ and to the Hurter and Driffield Memorial lecture (1926) of F. F. Renwick.¹¹ The latter suggests a determination of the apparent integral contrast of a paper calculated from tangents read at not fewer than ten equal intervals along the characteristic curve, covering the whole useful range of the paper. Figure 73 shows ten such points, the black spot in the middle indicating the average at which the contrast factor would be taken. A chart connecting negative ranges and contrasts of seven different grades of paper measured in this way is seen expressed in Fig. 74.

Development papers do not cover the entire range of tones in the subject. While Jones finds that chloride papers for amateur photo-finishing have a short scale of between 1:5 and 1:20, Renwick finds a 1:20 range for mat surface papers and as much as 1:50 for glossy. Reproduction of the tone values of a negative must necessarily be limited by the straight-line portion of the characteristic curve of the printing paper, and as the range of reflectance in this region is considerably less than the overall range, some sacrifice must be accepted at both ends of the scale.

The great attention now being devoted to the making of color prints on paper naturally introduces the problem of measuring colored images by reflected light. A step-wedge is used in the manner already described, but colored steps on Carbro, Chromatone or Wash-Off Relief paper are measured as *grays* by interposing in the light beam a filter of color complementary to that of the strip concerned. Thus in measuring a magenta strip, a green filter (minus magenta) would be interposed in the light beam or in the eyepiece. Such readings enable us to determine

the effect on gamma of variations in the pH of dye baths used in Wash-Off Relief; the effect of modifications in color toning, imbibition, etc., on density range, latitude and contrast; and the effects of concentration of dichromate in sensitizing carbon tissue; and so on. In the case of silver halide emulsions, tests coated on glass are of great additional value, as they are not obscured by the physical characteristics of the paper support.

COLOR-SENSITIVENESS. — An important field of investigation in the testing of photographic materials is the analysis or recording of their response to color. This must be done by exposing the emulsion to the various colors of the spectrum and measuring its response by the density recorded in different regions. It is somewhat unfortunate that anything in the way of a spectrograph or means of photographically recording color response should be so prohibitive in cost, when an excellent and moderately accurate instrument can be made with a little skill for a few dollars. The simplest form of spectrograph is probably that designed by A. K. Tallent, a diagram of which is seen in Fig. 75. Light from a lamp, *L*, is focused by a condensing

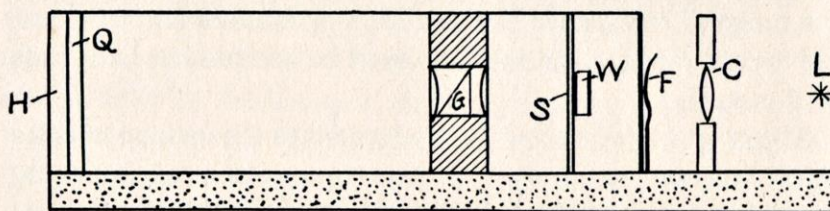


FIG. 75

lens *C*, on to a slit *S*, passing through a filter at *F* when desired, and through a small optical wedge, *W*, if wedge spectra are to be recorded. *G* is a prism-grating giving "direct-vision" dispersion so that an image of the spectrum falls upon a plate

or film in the holder, *H*. In front of the plate when exposed a wavelength scale, *Q*, can be thrown in.

The author designed many years ago a simple spectrograph capable of doing thoroughly good work, many of which have since been made and used in different factories for routine testing. For the information of those who wish to build such an instrument for themselves, the following particulars are given. The general design is shown in Fig. 76. A box of the

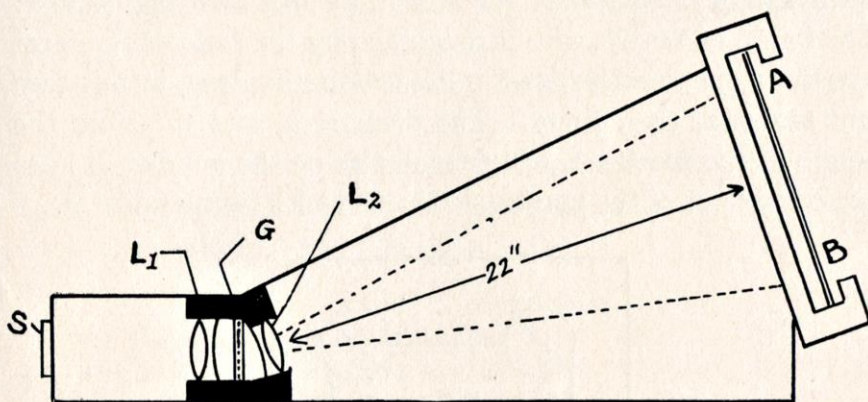


FIG. 76

approximate shape indicated is built up of seasoned mahogany about three-eighths of an inch thick. On a front about two by two inches, or a little larger, is mounted centrally the *slit*. A wooden block is made to take a short focus lens, L_1 . This may be a cheap achromat of about five and one-half or six inches focal length. Immediately behind it is fixed a diffraction grating replica. Celluloid casts of diffractions gratings, mounted on plane glass, are obtainable from Central Scientific Co. for as little as \$2.50. The size is 25 by 21 millimeters, and there are 5,900 lines per centimeter. The collimated light, parallelized by the slit being placed at exactly its own focal length from the lens, falls on the grating, the plane of which is parallel

to that of the collimating lens. The light, after passing through the grating, is diffracted, and will cast a first-order spectrum at an angle of about 18° or 20° on a screen, AB (in this case the emulsion); this must however be focused, and for the purpose an objective lens, achromatic of course, is fitted behind the grating in the manner shown, also at its own focal length from the plate plane AB . The longer the focus of this lens, the longer will be the spectrum, and a lens of sixteen to twenty-two inches focal length is suggested for a four by five inch plateholder. The image of the slit will be magnified by the ratio of the focal length of the objective lens to the collimating lens, in this case say $22/6$, or 3.66, times. The dispersion, and therefore the length of the spectrum, will depend also on the number of lines per centimeter of the grating, increasing with ruling fineness.

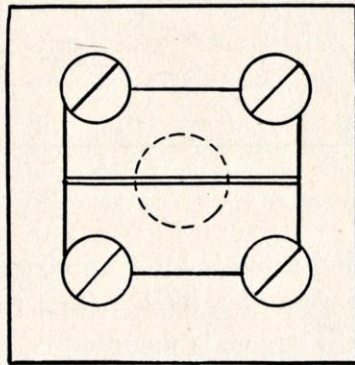


FIG. 77

A four by five inch plateholder is a very convenient size, and a back must be fitted to the camera body such that it can be slid along for successive exposures. A manufactured slit is an expensive item, though always worth-while; a homemade slit which will work remarkably well can be made in the manner indicated in Fig. 77. Two safety-razor blades, carefully paralleled, are screwed down over a central hole about three-quarters

of a centimeter in diameter, with flat-headed screws. For test work, the blades should be about a quarter of a millimeter apart. The camera back must be solid except for a slot slightly smaller than the spectrum, such as five-eighths or three-quarters of an inch wide and four inches long. Everything must be thoroughly dead-blackened, and to prevent scattered light from being reflected on the plate during exposure, it is a good plan to fit a piece of dead-blackened corrugated card along the bottom of the box.

Some sort of wavelength scale will be needed. This can be made as follows. A light source such as a carbon arc is focused by a condensing lens upon the slit, the poles being brushed with a solution of common salt, lithium chloride, a little calcium chloride, if possible a trace of thallos chloride, and a few drops of hydrochloric acid. A spectrum taken on a panchromatic plate will give the following lines:

Violet	Calcium	wavelength	394 m μ
	Calcium	"	396 "
Blue	Lithium	"	460 "
Green	Thallium	"	535 "
Yellow	Sodium	"	589 "
Orange	Lithium	"	610 "
Red	Lithium	"	671 "

Measuring the distances between the lines for the various wavelengths, a magnified scale can be drawn in India ink on Bristol board, and filled in for wavelengths from say 380 to 750 m μ . A great advantage of the grating over the prism for the dispersing medium is that the distance between lines is directly proportional to the difference between wavelength, as against the abnormal dispersion of the prism. As the plateholder is *flat* and not therefore equidistant along its entire length from the center of the objective, a slight loss of definition is inevitable. The scale is next photographed down, on a process plate, so that the spectrum lines fall in their right places. This is ascertained by

moving the negative over the focusing screen until the lines coincide. The scale when developed is cut out the exact size to fit easily into the slot in the back of the spectrograph, and mounted on a slider so that, when the plateholder slide is drawn, it can be pushed in as near to the sensitive film as possible.

It will be noted that many of the spectrograms published in this book and in current literature are of the *wedge form*. This is very useful, as, if a logarithmic wedge be employed, it gives a measure of the relative sensitivity at the different wavelengths. A small gray glass optical wedge can be mounted on the slit, or a neutral gray wedge can be obtained to fit over the wavelength scale or slot. If the slot is three-quarters of an inch by four inches, the wedge should be ordered the same size or a trifle longer, and graduating *across the width* from 0 to 2.5 or 0 to 3 density. In the latter case the transmission is 1 to 1/1000.

A simple, but useful bit of color-testing apparatus can be made with a printing frame and a rectangular step-wedge, across the steps of which are gummed a number of strips of gelatin filters, mounted side by side along the length of the wedge. Half a dozen such strips one-half inch wide and four and one-quarter inches long would be used in the case of a wedge three and one-quarter by four and one-quarter inches. A suggestion for the filters is:

	<i>Wratten No.</i>
Violet *	36
Blue	50
Blue-green	75
Green	74
Orange	58 + No. 15
Red	29

* All violet filters pass a considerable amount of deep red. This can be filtered out by the use of a liquid cell of weak copper sulphate solution, the concentration being adjusted by trial with the spectroscope so as to extinguish the red up to about 650 $m\mu$.

This will give a useful comparison of the relative color sensitivity of various materials, and of the relative sensitivity to individual colors of any particular material. Any such comparisons are of course affected by the efficiency or transmission factor of the various filters.

COATING WEIGHT. — It is important to be able to make a chemical analysis of the amount of silver or silver halide in a given area of plate or film. The following particulars are due to Eggert and Noddack. One square decimeter (ten centimeters square) of the coated film or plate is taken. It is put into a porcelain dish and fifty cubic centimeters of a hot ten per cent nitric acid solution is poured on it. To make this solution, ten cubic centimeters of concentrated nitric acid and ninety cubic centimeters of distilled water are mixed. When the emulsion is dissolved in the hot dilute nitric acid, twenty cubic centimeters of a forty per cent solution of caustic potash is run in. This neutralizes the nitric acid. It is of extreme importance that the nitric acid be *completely neutralized*, as the next step

is to run in thirty cubic centimeters of twice-decinormal $\left(\frac{N}{5}\right)$

potassium cyanide solution from a burette, stirring well. Any excess of nitric acid would liberate hydrocyanic acid at this stage, the breathing of which is usually fatal. It is for this reason that the excess of caustic alkali is first of all run in. When making up the standard solution of KCN, the cyanide should be weighed out in a room where the ventilation is good, and not in a stuffy darkroom, on account of the noxious fumes that it gives off.

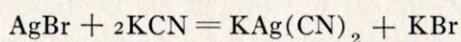
When the silver halide has gone into complete solution, the contents of the dish are transferred to a flask and the film or plate is rinsed several times with hot distilled water and the rinsings added to the contents of the flask. A further small

quantity of the potassium cyanide solution (2 cc) is then run in, and 3 cc of the following indicator added:

15 per cent solution of potassium iodide 50 cc
Ammonia (s.g. 0.910) 50 cc

The whole is then titrated back with standard decinormal silver nitrate solution until the end point — a faint persistent opalescence — is reached. A similar determination must be made with a blank; the difference between the blank and the actual titration gives the amount of silver (AgNO_3) equivalent in the sample.

When positive or reversal type emulsions coated at below eighty milligrams of silver halide per square decimeter are being estimated, it is advisable to use *two* square decimeters rather than one of the material. It should be remembered that potassium cyanide is not anhydrous, and should always be standardized against the silver nitrate solution. The reaction is:



The potassium cyanide should therefore be of 2 molar concentration, or thirteen grams per liter. But in view of the salt not being completely anhydrous, fifteen grams per liter may be used. If 15.74 grams of silver nitrate per liter be used in making the decinormal standard silver solution instead of 17.0 grams, the titration will read directly in milligrams of metal.

In making pH determinations of coated film, a definite area of film is cut into pieces and soaked in freshly distilled water and the water tested against a similar quantity of freshly distilled water as a control. Colorimetric tests can be made with an indicator having a range somewhere between 5 and 8 pH; or if necessary, two tests may be made with indicators each of half the range. For tests of dyed or colored materials, an electrometric apparatus such as the Beckman is necessary; in England portable apparatus is made for pH determinations by

the Cambridge Instrument Co. Owing to the rapidity with which even freshly distilled water decreases in pH in the atmosphere of big manufacturing towns and cities, the water used should preferably be freshly distilled a few minutes before the test is made.

KEEPING TESTS. — An estimate of the probable keeping quality of sensitized materials is of importance in laboratory work and is essentially part of the ordinary routine in commercial production. It might be imagined that the faster the emulsion is, the poorer would be its keeping qualities. This, however, is not always the case, some slow emulsions being troublesome in this respect. Thinly coated plates are liable to go off at the edges (to fog round the edge on development without exposure), and any products which have given evidence of slight fog on testing after being emulsioned must always be regarded with suspicion. There is a tendency for any emulsion that has been pushed too far for speed, or over-heated, to give veil, but reference to this will be made again in Chapter XIV. The veil, or fog, must be deducted from all readings in sensitometric work, and for a practical test the developer that is recommended for use with the material should be used in making that test.

While a slow positive or process emulsion should not, on normal development without exposure, give a higher fog reading than 0.02, that on an ultra-rapid emulsion may legitimately be of the order of 0.1. On keeping for any length of time, the fog reading usually increases, especially if the material is stored under warm or humid conditions, and in order to get an estimate of the *life* of the product, it is common practice to subject it to an oven test. The material, wrapped in the packing which it is intended to use, is kept in a thermostatically controlled hot air or water oven at a temperature of 105° or 110° F. for about ten days. It will then have developed approximately the same amount of fog as would be anticipated from, say, six months'

storage in the average dealer's stockroom. The humidity of the oven is an arbitrary matter, but 55 to 65 relative humidity is suggested as being fair.

When making fog tests, it is customary to pack the material in two halves, one being kept in the oven, the other being kept at room temperature, under the best possible conditions. The initial laboratory tests will, of course, also have been made for reference. After the period of ovening or "incubation," the control and the oven samples are developed together in total darkness and fixed, and the fog readings compared. A sensitometric test will also reveal any loss or gain in speed or alteration in the development factor.

While at first sight keeping tests seem simple and straightforward enough, they are complicated by the fact that when material is stored in an oven, the sides, top and bottom of the inside of the package do not necessarily experience the same conditions. An elaboration of the tests is to place the packages in a cage which rotates in the center of the oven; many other suggestions have been made. Highly red-sensitive and infrared emulsions, owing to their natural reaction to the longer wavelengths, are apt to develop fog in warm climates quicker than color-blind varieties.

The oven test is invaluable in checking up on wrapping materials. No wrapping papers, nor cardboard boxes, should be accepted for the packing department's use unless and until they have been demonstrated by an oven test to be harmless in the way of fog production. In the case of rollfilms which are merchandised in aluminum containers, sealed or unsealed, the oven test should be made with the spooled films in these, so that absolutely practical conditions are obtained. Materials destined for tropical work or expeditions which are to be supplied in soldered tin boxes should again be submitted to an oven test so packed, the reason being that at 110° F., or thereabout, a

certain amount of moisture may be evolved in which the sensitized materials may show some alteration.

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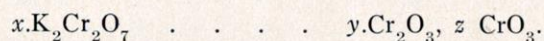
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CHAPTER XIII

VARIOUS METALLIC PROCESSES

Carbon and Carbro Tissue — Gum-bichromate — Iron Printing Processes — Ferroprussiate — Cyanotype — Kallitype — Platinotype and Palladiotype — Diazotype Papers — Bleach-out Color Processes

THIS method of printing depends upon the action of light upon a dichromate in the presence of organic matter. The response to light was shown by Cartwright¹ to be most active in the region between 350 m μ and 420 m μ . Attempts have been made by Ronald Trist and others to sensitize dichromated gelatin or fish glue to green and red rays by color-sensitizing, without particular success. On exposure to light in the colloidal medium, the dichromate is converted into a brown chromochromate consisting of uncertain proportions of chromic acid and the green oxide of chromium:



According to Eder, the insoluble image consists of gelatin in combination with chromium oxide, while Lumière and Seyewetz found that under normal conditions the proportion of chromium oxide combined with the gelatin is considerably higher than that which combines with gelatin treated with chrome alum in the ordinary way. The exposed dichromated gelatin swells much less in cold water, and is insoluble in hot water. So the printed image, on washing with hot water, consists of insolubilized gelatin with the unexposed *soluble* gelatin removed.

It was found by Abney that the insolubilizing action of light continued after a short preliminary exposure, indicating the formation by the action of light of a photo-catalyst,² which continues the tanning action by reaction with the excess of dichromate and colloid. Unfortunately, sensitized "tissue," as

paper coated with the gelatin and dichromate is termed, rapidly becomes insoluble on keeping in the dark, and hence it is customary, in fact necessary, in manufacturing practice to supply the gelatin-coated paper which merely has the necessary dye or pigment incorporated with it. Some firms supply sensitized tissue, but it will keep in good condition for only a very limited time.

Owing to the important property, possessed by dichromated gelatin, of giving an almost perfect scale of reproduction, the carbon process and its ally, Carbro, give unsurpassed three-color prints from a correctly balanced set of separation negatives. The carbon process is largely responsible for the excellent tone reproduction in photogravure, and its use for this process makes it an important item in manufactured products.

Carbon tissue is paper coated with a mixture of gelatin and pigment, which the user sensitizes shortly before use by immersion in a solution of potassium or ammonium dichromate which may be varied from one per cent for weak negatives to six per cent for vigorous negatives. In making the tissue, a moderately hard gelatin which does not swell excessively should be selected, as soft gelatins have a tendency to wash out too easily in development. Heinrich's hard emulsion gelatin or a comparable American variety can be recommended. The raw paper selected should not be too highly sized, but well calendered. For experimental work, a plain smooth paper such as is used as wallpaper for covering ceilings will be found very suitable.

An advantage of the carbon process is, of course, that any suitable pigment can be used which is fast to light, so that prints can be made in any color. This is of especial importance in natural color photography, since coloring matter can be used which complies with theoretical requirements as regards spectral composition. Thus yellow, magenta and blue-green papers are probably the types most demanded at the present time. For small-scale work the moist water colors supplied by art dealers

238 PHOTOGRAPHIC EMULSION TECHNIQUE

in collapsible tubes make good media, although certain pigments may be found to react with the dichromate, causing insolubilization without exposure.

For commercial mixings, these formulas are suggested:

<i>Sepia</i>	Burnt sienna	90 parts
	Lampblack	10 parts
<i>Warm black</i>	Chinese white	25 parts
	Vandyke brown	40 parts
	Carmine	40 parts
<i>Brown-red</i>	Indigo red	40 parts
	Chinese white	35 parts
	Alizarin red	25 parts

Prussian blue and indigo are largely used also. The pigments are weighed out and mixed with an equal weight of water, and five per cent of the total weight of glycerin is added. The mixture is well ground in a color mill, and then added to twenty times its weight of the following:

Gelatin	125 g
Water	1000 cc
5 per cent alcoholic solution of phenol	50 cc
Soft soap	20 g
Sugar	25 g

After thorough mixing, the bulk is filtered at a temperature of 105° F. (40° C.), and coated on a paper-coating machine, preferably by kissing roller.

A formula for black tissue given by Clerc³ is:

Gelatin	500 to 800 g
Cut sugar	100 to 200 g
Salicylic acid	2.5 g
Vegetable black	100 g
Carmine	10 g
Indigo	5 g
Glucose syrup	100 cc
Water	2500 cc

For preparing a ready-sensitized tissue, fifty grams of potassium dichromate and ten grams of potassium citrate would be added, first dissolved in 250 cc of water, to which sufficient stronger ammonia water has been added to change the color from orange to pale lemon-yellow. Such tissue must be used within three or four days.

The sensitized tissue is printed under the negative and soaked in cold water, then brought into contact (under the water) with a sheet of either temporary or permanent transfer paper. If single transfer paper is used, the image naturally becomes reversed in the process. Such paper may be coated with:

Medium viscosity gelatin	50 g
Water	1000 cc
5 per cent chrome alum solution	10 cc

The addition of 250 cc of a twenty per cent alcoholic solution of shellac will provide a mat transfer paper. The support paper and printed tissue, when withdrawn from the cold water, are squeezed firmly together and allowed fifteen to twenty minutes between blotting boards before they are immersed in warm water, pulled carefully apart, and the unexposed coating washed away from the transferred image.

The image may be developed out on a temporary support, which may be paper coated with shellac and rolled, or some material such as celluloid, aluminum sheet, sheet indiarubber, etc., first prepared with a waxing medium. The temporarily transferred image is re-transferred to a final support, which may be a paper coated with the formula above given, but the weight of paper base should be heavier.

Plain slightly subbed nitrate or acetate base coated with a seven or eight per cent solution of gelatin containing no chrome alum may be sensitized with dichromate and used for making three-color prints from separation negatives. A slow bromide

emulsion with no hardening agent may be coated on film base for the same purpose. The silver salt plays no part in the process, but makes the image much more plainly visible in printing, and more controllable. Two minutes' immersion in a three per cent solution of potassium or ammonium dichromate will suffice for sensitizing, and this can be done in yellow light. The material is printed *through* the base (the gelatin or emulsion side away from the film of the negative), and after exposure the image is developed in hot water of about 160° F. (72° C.). Washing-out must not be too vigorous, as a very thin film of gelatin should remain over the faintest highlights. If a bromide emulsion has been used, the film must of course be fixed after washing out, and finally well rinsed. Such gelatin relief images can be stained up with appropriate dyes and mounted in register as three-color transparencies.

GUM-BICHROMATE.—While the image from a negative printed upon carbon tissue must be transferred to another base to be developed, a mixture of coloring matter with gum arabic, sensitized with dichromate, can be applied to paper, and the dry paper exposed under a negative in daylight and developed with cold water without any transfer. The unexposed gum-pigment remains completely soluble and washes away, while the exposed parts remain and provide the image. The gum-bichromate process, as it is familiarly known, is very suitable for prints of bold subjects, especially in the larger sizes, but does not lend itself to the reproduction of fine detail. The carbon process, on the other hand, is capable of yielding the finest detail, as is evidenced by its application to photogravure, where halftone screens of 150 to 175 lines to the inch are used.

Gum arabic is best crushed into small pieces and suspended in a muslin bag in distilled water; it takes some time to dissolve, but the dirt ordinarily present in the gum will remain behind in the bag. The gum should be dissolved in about one

and one-half times its weight of water. To one hundred cubic centimeters of such mucilage is added:

Potassium dichromate	10 g
Water to make	100 cc

To such a mixture sufficient pigment is added to give a coating — when applied with a brush to paper — of a density which will allow the finger to be seen through the paper when examined by transmitted light. In other words, the tint applied to the paper should be considerably less than that required to form the shadows of a print. Rouge (iron oxide), lampblack, burnt sienna, Prussian blue, indigo, and alizarin red, being inert to the chemicals employed, are the best pigments to use. Another formula for gum-bichromate is the following:

Gum arabic solution 1:1	50 cc
Ammonium dichromate, 10 per cent solution ...	100 cc
Pigment	25 g

The prints are best developed by floating face down on cold water, and gently washing out until the whites are clear. Five minutes in a five per cent solution of potassium alum before the final wash will render the film hard.

IRON PRINTING PROCESSES. — Iron forms two principal types of salts, ferric and ferrous. The ferric salts are combined with half as much again of the acid radical as the corresponding ferrous salts. The action of light upon the ferric salt of an organic acid was early noted, and is to reduce it to the ferrous state; an iron process was based on this phenomenon in 1842 by Herschel, who used the ferrous compound to react with ferricyanide and form a permanent image. Ferric citrate and ferric oxalate are reduced respectively to ferrous citrate and ferrous oxalate; similarly potassium ferricyanide, $K_3Fe(CN)_6$, is reduced to ferrocyanide, $K_4Fe(CN)_6$. These ferrous salts form many highly colored pigments by reaction with salts of other

metals with which they form insoluble ferrocyanides, best known of which is Turnbull's blue. If paper sensitized with a ferric salt is exposed under a negative and developed with a suitable reagent, a permanent colored image will result; the most familiar example is the engineer's blueprint; this is made on paper sensitized with a mixture of a ferric salt and potassium ferricyanide. Printed under a design or translucent drawing until the lines appear of a light brown color, a mere wash in cold water will effect the reaction and leave a deep blue image of ferrous ferrocyanide.

This process, known as ferroprussiate or cyanotype, is used on a very large scale, although it has experienced some competition in recent years from the vapor-developed diazotype papers to which reference will be made later. The sensitizing solution can be applied in strong yellow light, and any good quality, pure paper can be treated. It offers the simplest possible method of printing photographs, and can be applied to printing on cotton or linen fabrics; these, if printed and developed in water in the usual way, can be toned to a beautiful violet or purple by treatment with a boiling solution of alizarin.

The paper is usually prepared with ferric ammonium citrate, which may be obtained in the form of brown or green scales. The green scales have the average composition of $(C_6H_5O_7)_2Fe_2(NH_4)_3$, while the brown scales are $(C_6H_5O_7)_2H_2Fe_2(OH)_3(NH_4)_3 \cdot 3HO$. Valenta found that the green compound gave very much quicker printing with brighter blue images. A reliable formula for a sensitizing solution is:

A. Potassium ferricyanide	40 g
Water	250 cc
B. Green ammonium ferric citrate	95 g
Water	250 cc

If the brown citrate is used (which is claimed to give rather better keeping quality for manufactured ferroprussiate paper),

the quantity may be increased to 110 g, and the water in *B* increased from 250 to 500 cc. The latter sensitizer also gives greater contrast and is useful for copying plans, tracings, etc., while the first formula would be preferred for photographic prints. The two solutions are mixed, filtered, and used cold. It is very important that the mixture is orange-brown colored and not *green*. It is advisable to use large crystals of potassium ferricyanide and before weighing them to rinse them with a little distilled water; this will remove any yellow ferric salt with which they may be surface-contaminated. The salt should be dried on filter paper after rinsing, before weighing. If stock solutions are made up, a trace of sodium formate may be added to prevent the formation of mold.

Another formula, suitable for coating larger quantities, provides for a mixture of stock solutions:

25 per cent solution of ferric ammonium citrate	400 cc
15 per cent solution of potassium ferricyanide	150 cc
10 per cent solution of citric acid	300 cc

The ferric ammonium citrate should be freshly made, and paper sensitized with the formula will keep in good condition for two to three months if stored in a dry place. The addition of phosphoric acid to the sensitizing solution has been suggested to stabilize the lines and the blue background.

For commercial manufacture, sensitizing by dipping will be found suitable practice. In the laboratory, the solution can be applied with a wad of cotton about the size of a golf ball tied with thread to the end of a glass rod. A wide soft brush may also be used. The paper is laid out on a flat board or piece of thick cardboard and held down at the four corners by pieces of scotch tape. It is then brushed over as evenly as possible. The board is best inclined to the table at an angle of about thirty-five degrees. In machine coating, an excess of

solution is applied, and the paper wiped by a doctor just beyond the coating roller, leaving the desired thickness evenly applied. Commercial coating weight is about 60 to 65 g of iron salts per 100 square meters — roughly one grain to the square foot. The coated paper should be dried in total darkness.

Printing is best done in sunlight, though arc or mercury vapor is satisfactory. Ferroprussiate paper gives a deep blue image on a white ground, and of course gives a “negative” of a line drawing, white lines on a blue background. If, on the other hand, blue lines are wanted on a white background, this effect can be obtained by coating with a solution of gum arabic sensitized with ferric salts, and after printing, developing it with a ten or twenty per cent solution of potassium ferrocyanide, on which it is usually floated. An alternative method, given by Pizzighelli,⁴ admits of simple development by washing in water; the sensitizing solution is as follows:

20 per cent solution of gum arabic	200 cc
50 per cent solution of ferric ammonium citrate	80 cc
50 per cent solution of ferric chloride	50 cc

On mixing the above, a very viscous solution is produced, but after standing for a few hours it disperses and becomes thin enough to be applied with a brush or wad of cotton. As this paper is considerably more sensitive to light, it should be made in yellow safelight and dried in complete darkness.

KALLITYPE PAPER. — This is printing paper sensitized with ferric oxalate, which is reduced by the action of light to the ferrous state; the strong reducing action of the ferrous salt is then used to develop a silver image, but, owing to its insolubility, the presence of an organic salt such as potassium oxalate is required to act as a solvent. The printed paper may be put into a bath containing silver nitrate, or the silver — or part of it — may be incorporated in the sensitive coating. The simplest

means of sensitizing is to use a composite solution such as the following:

Ferric oxalate	22.5 g
Potassium oxalate (neutral)	5.5 g
Silver nitrate	5.5 g
Distilled water	100 cc

A smooth, thin drawing or water color paper or plain raw photographic paper is first sized with a paste made by mixing three grams of starch with a little water until smooth, and then stirring while sufficient boiling water is added to bring the bulk up to two hundred cubic centimeters. This solution is boiled for five minutes, cooled and poured into a beaker or crock. When cold, a skin will be found to have formed on it. This is removed, and the liquor is strained through a piece of washed muslin into a clean dish. The paper is best coated by floating, unless a small coating machine such as has been described elsewhere is available.

When dry, the paper is printed in daylight until the shadows are just visible, and is then developed with an alkaline solution of Rochelle salt. A basic formula is:

Warm water	500 cc
Rochelle salt	30 g
Borax	15 to 25 g
10 per cent solution of potassium dichromate ..	5 cc

The full quantity of borax gives black tones, a smaller amount giving warmer tones.

When printing from weak negatives, a slight increase in the proportion of dichromate may be used. If the contrast is too high, the print can be removed from the developer and transferred to a separate bath containing no dichromate. When developed to completion, the print is fixed in a two and one-half per cent solution of plain hypo rendered just alkaline by the addition of a few drops of ammonia. An attractive feature of

kallitype is that the image can be toned afterwards with a gold bath, such as is used for printing-out paper, or with platinum or palladium.

PLATINOTYPE. — The successful results obtained with kallitype led W. Willis in 1878 to substitute platinum for silver, and so to produce what still remains the finest printing medium available to photographers — platinotype. Prints made by this process have an exquisite range of gradation. The image is absolutely permanent. If we take the tone range of a contrasty chloride paper as 1:10 and of a good bromide paper as 1:50, then we may justly say that the gradation of platinotype is 1:100.

The paper itself, needless to say, must be of pure quality, and especially free from iron spots or specks. It must not be sized with an animal (glue) size, though a first coating with a one per cent solution of the purest emulsion gelatin may be applied. A three per cent solution of arrowroot, boiled and filtered, is better. The paper may be immersed in the solution for five to twenty minutes, according to the surface, and then dried slowly in a cool atmosphere.

For sensitizing, three stock solutions are prepared:

A. Potassium platinum chloride	1	g
Water	6	cc
B. Ferrous oxalate	1	g
Water	4.5	cc
C. Ferrous oxalate	10	g
Potassium chlorate	0.2	g
Water	45	cc

For sensitizing, mix 5 cc of *A* and 3 cc of *B*; add 2 cc of *C* and 4 cc of water. For contrasty negatives, the *C* solution may be omitted and equal parts of *A* and *B* only used. The sheets of sized paper, cut to size, should be laid on a sheet of clean glass or in the bottom of a porcelain dish, and the sensitizing mixture

applied as evenly as possible with a soft camel's hair brush. This may be done in Mazda light.

Paper prepared as above described is printed in sunlight until the dense shadows are of a light orange-brown color; no details should be seen in the extreme highlights. The print is developed with a hot solution, 100° to 180° F., of:

Potassium oxalate (neutral)	300 cc
Oxalic acid	5 g
Water to make	1000 cc

Alternatively, cold development may be used if the sensitizing bath be somewhat modified as follows:

A. Solution as in above formula.	
B. Ferric oxalate	10 g
Lead oxalate	0.5 g
Water	45 cc
C. Potassium dichromate	1 g
Water	10 cc

4 cc of *A* is mixed with 6 cc of *B*. To this mixture is added 10 drops of *C* mixed with 3 cc of distilled water.

A printing-out platinum paper for giving a visible image can be made as below:

<i>A</i> solution as above	4 cc
50 per cent solution of sodium ferric oxalate ..	6 cc
50 per cent gum arabic solution	4 cc
<i>C</i> solution as above	5 drops

Paper sensitized by brushing it over with this solution (after the usual sizing) is printed fully out, and then finished off by washing or placing between wet filter papers. All platinum papers should be given several final rinses in water acidulated with one or two per cent of hydrochloric acid.

Owing to the difficulty of making entirely satisfactory platinotype papers in the laboratory, Clerc recommends⁵ the easier

248 PHOTOGRAPHIC EMULSION TECHNIQUE

procedure of sensitizing the paper with ferric salts and using the platinum compounds in the developing solution. The sizing solution recommended is:

Gelatin	8 g
Water	1000 cc
When melted and dissolved, add	
Potassium alum	2 g

The paper is floated on this solution, used hot, and the upper surface (hereafter the back side) should be marked with a pencil. The sized paper is brushed evenly with the sensitizing bath below:

Ferric oxalate	25 g
Oxalic acid	2 g
Lead oxalate	1 g
Hot distilled water to make	100 cc

The lead oxalate may be made by mixing equal volumes of a ten per cent solution of lead acetate and a four per cent solution of oxalic acid, filtering and washing the white pasty precipitate left in the filter paper several times with distilled water. The image on printing is much less visible than in the case of the papers previously described, and can be judged only by experience or by comparison with some form of print-out actinometer. The developing solution, containing the platinum salts, is made thus:

Stock Solution

Potassium oxalate (neutral)	200 g
Di-sodium phosphate	50 g
Water to make	1000 cc

To 20 cc of this stock solution is added 2 cc of a ten per cent solution of potassium chloroplatinite. Development is done with a flat camel's hair brush, moved over the image " with a quick light movement, dipping it in the developer for each

stroke so as to insure equal and uniform action of the solution." When evenly coated with developer, it is left until completely developed, fixed in weak hydrochloric acid, and washed.

Owing to the high cost of platinum, palladium has been used on an increasing scale. Palladium salts may be substituted for platinum in many of the above formulas, particularly in developing formulas where the paper itself is sensitized only with the iron salts.

PRINTING WITH COPPER SALTS. — A formula for sensitizing with copper salts has been suggested by Thiebaut⁶ for use on paper previously substratumed with gelatin:

Potassium dichromate	90 g
Copper sulphate	50 g
Water to make	1000 cc

The paper is exposed in daylight until the highlight detail is clearly visible, and is then developed in a five per cent solution of anilin hydrochloride acidulated with sulphuric acid. Green images are given by this process.

URANIUM PAPER. — This is prepared by the application to *unsized* paper of:

Uranyl nitrate	16 g
Water to make	100 cc

The suggestion has been made of adding four grams of copper sulphate to this solution. It is printed in daylight, preferably under a vigorous negative, and developed with a five to eight per cent solution of potassium ferricyanide. Warm sepia or brown images are given by the process, and various metallic toners can be applied.

DIAZOTYPE PROCESSES. — Methods of photographic printing have been successfully based on properties of certain aromatic diazo compounds which become bleached on exposure to light. The unexposed parts remain unaltered, and on development

with an alkali, or with ammonia vapor, an image remains consisting of a permanent azo dye, thus giving a positive image from a positive original.

In the Feertype process,⁷ on the other hand, a dye is formed in the exposed portions of a diazo compound which can be developed in acidulated water. A sensitizing formula of this nature is as follows:

Iso-sodium toluol diazo sulphonate	25 g
Beta naphthol	25 g
Sodium hydroxide	8 g
Water	1000 cc

In Ozalid paper,⁸ Koegel produced positive from positive prints in purple lines on a slightly colored background. The paper was impregnated with a solution of a diazo-anhydride and resorcin equilibrated with tartaric acid. The diazo-anhydride is decomposed by light, but the unexposed material is converted to an intense purple-brown on exposure to ammonia vapor. The fact that the paper is developed dry eliminates distortion. Under the name of Ozafilm, diazo compounds have been introduced into viscose for sub-standard motion picture films, having a thickness of only a thousandth of an inch, so that the bulk of the reel can be greatly reduced.

More recently, chinonazide has been used as a sensitizer; this compound is diazotized para-aminophenol, which under the action of light becomes converted into hydroquinone. If the paper, after printing, is treated with a weak solution of silver nitrate, a latent image is formed which can be physically developed with a metol-sulphite-silver bath.

On exposure to light a diazo compound loses its faculty of coupling with a coupling component, being probably decomposed into a phenol. In those parts where the light has not acted, and the diazo retains its original composition, it is able to form an azo dyestuff by the combined action of the coupling

component and an alkali.⁹ In the simplest case, the coupling component can be mixed with the diazo compound, when, after printing, development can be carried out with ammonia vapor. An alkali can, on the other hand, be mixed with the azo coupling component. An example of such a sensitizing solution is:

p-amino-dimethyl anilin hydrochloride, diazotized with nitrous acid	20 parts
Tartaric acid	2 parts
Barium chloride	100 parts
Water to make	1000 parts

Paper sensitized with the above is printed and developed with a weak alkaline solution of β -oxynaphthoic acid anilide. This gives a black image on a white background.

Another formula is as follows:

para-amido-ethyl anilin hydrochloride, diazotized with nitrous acid	20 parts
Potassium citrate	0.5 part
Barium chloride	100 parts
Water to make	1000 parts

This gives a dark brown image on development with an alkaline solution of β -naphthol. The barium chloride prevents bleeding of the developed azo dyestuff; the use of a catalytically acting substance called an anti-oxygene such as pyrogallol or meta-phenylendiamin has been suggested by F. van der Grinten.

PRINTING-OUT NATURAL COLOR PAPERS. — Very little information is available as to the preparation of sensitive coatings of fugitive dyes with which direct printing-out effects can be obtained from natural color transparencies, yet this is a field for experiment which may well see immense developments. It was noted by Grothuss that certain dyes were destroyed by the light radiations which they absorbed; in other words, a fugitive magenta dye would be bleached by green light, a blue dye by yellow light, and so on. A black mixture of blue-green, magenta,

and yellow dyes applied to paper and printed out under a color transparency would yield a color print.

Bleach-out color papers were made by Neuhauss, Worel, and others, but they were too insensitive to be of practical value; J. H. Smith, however, succeeded in producing a black bleach-out paper which gave a fairly creditable print from an Autochrome in one to three hours' exposure to strong sunshine. The author at one time experimented with Dr. Smith to employ arc light printing, but the speed did not justify the continuation of the work. Also the bleach-out images, though fixed in various ways, were not by any means permanent.

An example of possible advance in this direction may be seen in the very marked increase in light-sensitivity of methylene blue if used in the presence of certain thiourea derivatives. Three dyes of the subtractive colors sensitized in a similar way and balanced so as to bleach out at equal rates after allowance had been made for the relative transmissions of the primary colors of the transparency, would yield a natural color printing medium, provided the sensitizers could be destroyed after printing, and the remaining dyestuffs rendered reasonably permanent.

Indirect processes employing more light-sensitive coatings which would, under the influence of light, react in turn with the dyes and destroy them, figure among present attacks on the problem.

Chapter References

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CHAPTER XIV

EXTREME-SPEED EMULSIONS

Super- and Hyper-sensitizers — Sulphur Compounds in Gelatin — Anti-fogging Agents — Speed Characteristics

IN considering the faster emulsions which have been recently introduced, one is tempted to raise the old question: "What is speed?" It has already been seen in Chapter XII that if the toe of the characteristic curve of a fast emulsion is sufficiently straight to permit of the whole tone range being recorded on it, that is, provided that such density range as it offers will suffice for the work in question, a very much higher effective speed is obtained than with the same emulsion developed to a higher gamma and the upper straight portion of the curve used. Similarly if the free bromide be removed from the emulsion, the whole curve may rise from AB to $A'B'$ (Fig. 78), the speed being thereby raised from $\frac{K}{OC}$ to $\frac{K}{OA'}$. If therefore

the need for free bromide could be dispensed with by the use of an anti-fogging agent, an immediate rise in speed could be obtained. The removal of the bromide is substantially what happens when a plate or film is "hyper-sensitized" by bathing.

The line of thought which actuated many emulsion-makers in the stage intermediate between the first really fast orthochromatic and panchromatic emulsions and the more recently introduced extreme-speed variety may be gathered from a comparison of the two following formulas, one of which was published as an indication of how the other basic one might be "pushed" for greater sensitivity:

	<i>Fast</i>	<i>Extreme</i> <i>speed</i>
A. Potassium bromide	120 g	132 g
Potassium iodide	3 g	4.5 g
Gelatin	50 g	30 g
Water	1200 cc	1000 cc
Erythrosin 1:1000	— cc	50 cc
B. Silver nitrate	150 g	150 g
Water	600 cc	500 cc
Redissolve.		
Temperature of reacting solutions ..	30° C.	40° C.
Emulsifying time	rapid	slow, taking 6 minutes
Ripening time	25 to 40 minutes	30 to 50 minutes
Ripening temperature	40° C.	50° C.
Bulk gelatin	120 g	140 g

The gelatin is soaked for half an hour, drained and remelted, and added at 45° C. in each case; after ten minutes' stirring, the emulsions are set in ice water. The fast emulsion is washed next day, the extreme speed one, after keeping at 3° to 8° C. for two to three days. In the case of the extreme speed emulsion, further gelatin may be added again after washing; the emulsion is then warmed to between 40° and 42° C. and stood in a room at about 22° C. for two to three hours.

It will be recognized that this difference really amounts to a gentle push all the way around. With a well-selected gelatin, the speed may be raised from say 650 to 1500 H and D in this manner, but the author's experience of forcing an emulsion on these lines is that it is liable to yield variable results, and that some of the best emulsions so prepared, which are perfectly clean at the time of making, turn out disappointing from the keeping standpoint, developing fog and steadily losing speed.

A good deal of progress in the direction of speed has been

made as the result of more critical testing of gelatins. One example of this, of outstanding importance, is the fact that by giving a sufficiently long digestion, what had hitherto been regarded as a "slow" gelatin may be made to give the speed of a "fast" sample. This digestion may have to be very protracted, lasting for many hours instead of from twenty minutes to an hour or so. But the time-factor appears to be of vastly more importance than had been previously recognized.

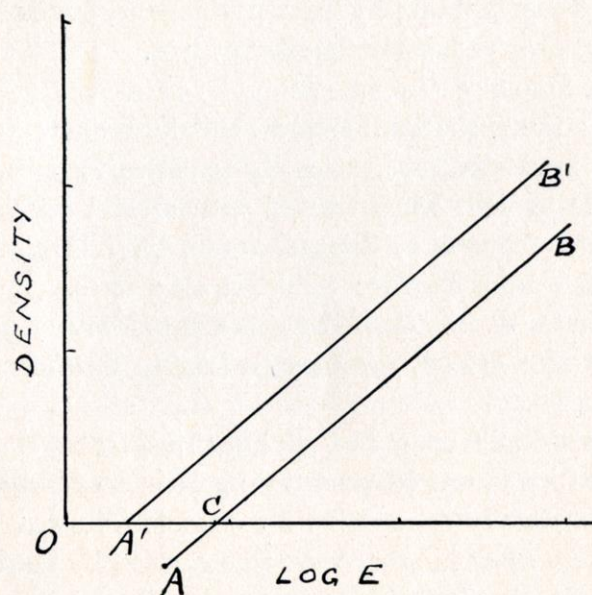


FIG. 78

As stated elsewhere, the great advance in panchromatizing-dye chemistry has given a fictitious but perfectly practical increase in speed to some color-sensitive negative emulsions, the response to light of the longer wavelengths making an important addition to their sum total of response. The discovery that certain dyes act as super- or hyper-sensitizers, greatly increasing the sensitivity induced by another dye the color-sensitizing region of which they do not affect, has given another jump in

speed, of important practical value, although the phenomenon looks at first sight a little like perpetual motion.

The great rapidity of recently introduced emulsions can be ascribed largely to the use of stabilizers, the addition of which to an emulsion in the making renders it possible to force the speed or to add "sensitizers" without pushing a proportion of the grains too far and rendering them developable without exposure as "fog." An instance is the use, suggested by Kendall,¹ of a 2-mercaptan-4-hydroxy-pyrimidene, or one of its alkyl, aralkyl or aryl substitution derivatives.

We must to some extent associate color-sensitizing with hypersensitizing; the carbocyanins and similar products in general use, as we have seen, are extremely sensitive to light, but become stable to light when treated with certain derivatives of thiourea; yet thiourea or thiocarbamide, $\text{CS}(\text{NH}_2)_2$, by itself, is one of the most effective emulsion sensitizers. The choice of sensitizer must obviously be coordinated with that of the color-sensitizer; indeed, one may be largely dependent on the other.

The sensitizing property of allyl isothiocyanate, $\text{H}_5\text{C}_3\cdot\text{NCS}$, which as we know was isolated from gelatin by Sheppard, and shown to be chiefly responsible for emulsion "speed," cannot be used *ad libitum*; in other words we cannot, by doubling the quantity used, obtain double the speed. Indeed, for many years after the publication of the function of allyl isothiocyanate, the general speed of plates and films went up very little, and such advances as were made were *not* directly due to its exploitation. Allyl isothiocyanate is the essential oil of mustard, and can be obtained by macerating black mustard seeds with water, after first removing the fixed oil, then distilling. When mixed with ammonia and subjected to ammonia gas, it yields allyl thiourea or thiosinamin, $\text{NH}_2\text{NH}(\text{C}_3\text{H}_5)\text{CS}$; this is a weak base, soluble in water, alcohol and ether.

A test for these sulphur compounds in gelatin has been given by Luther,² who suggests the use of a solution of twenty to twenty-five per cent of caustic soda (sticks) in 100 cc of distilled water, in which 3 to 4 g of pure lead nitrate has been dissolved. One volume of this alkaline lead nitrate solution is mixed with one volume of a fifteen to twenty per cent solution of the gelatin to be tested, and placed in a test-tube in a boiling water bath. A good quality gelatin (containing the most useful proportion of sulphur compounds) will show a brown coloration after about half an hour, which will remain visible after one hour.

Selenium compounds have been largely investigated, for their uses both as sensitizers and as anti-fogging agents. Thus addition of an α -thione or α -selenone of a heterocyclic nitrogen compound such as thiazole, quinoline, pyridine, etc., has been suggested for speed-sensitizing, while the incorporation of a sulphinic or seleninic acid or soluble salt of either has been used as a stabilizer against fogging.³ Amino-purines have been suggested for the same purpose, that is, stabilization. A compound of the purine series has also been employed, containing a hydrogen atom which is replaceable by silver attached to a nitrogen atom, when promoting *ripening* by means of a sulphur compound.

While a very large number of patents have been granted since about 1933 for the protection of color-sensitizers, color hyper- or super-sensitizers, and emulsion sensitizers and stabilizers or anti-fogging agents, there must always remain a clear field for experimentation and further research. The addition of any extreme-speed sensitizer must first be tried out with a few pre-selected gelatins, among which an iso-electric sample may well be present; sensitizers which promise success must then be tested in conjunction with anti-fogging or fog-retarding compounds, until a suitable balance is obtained. The sensitizers

may or may not be intimately associated with a color-sensitizer in the case of panchromatic emulsions. The final emulsion may be further assisted by appropriate buffering, which may well be made to function in the undercoat of a slower, stable emulsion in the case of double-coated film stock.

The H and D speed of modern emulsions, while it increases with prolonged development, appears according to Trivelli and Smith ⁴ to reach a breaking point long before the gamma has reached its maximum value; beyond this point the speed diminishes. This is an important point, as although the observation applies to some extent to older-type emulsions it emphasizes the necessity for careful sensitometric testing of a super-speed emulsion in order to determine the conditions under which its optimum speed can be realized.

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INDEX

A

Abney, W. de W., x, 115, 236
Acetate film base, 175
Agar-agar, 2
Agfa color plate, 81
Air conditioning, 151
Alcohol, 35, 49, 153
Allyl isothiocyanate, xi, 256
 thiourea, 256
Ammonia, 8, 32, 67, 69, 78, 93
Arago, 1
Arlex, 173, 184, 185
Auramin, 107
Autochrome plate, 81, 82

B

Baker, T. T., 83, 97, 131, 132, 215,
 227, 252
Baryta coating, 157
Bathing of plates and films, 110
Bayley, R. Child, 25
Beckerel, 23
Bipack emulsions, 121
Bleach-out papers, 251
Blending emulsions, 77
Bloch, O., 203
Bogue, R. H., 21
Boiled emulsions, 6
Bolton and Sayce, 2
Breaking up emulsions, 70
Buffering of emulsions, 72
Bulk gelatin, 22
Bunsen and Roscoe, 19

C

Cadett, James, 149
Capstaff density meter, 218
Carbocyanins, 116

Carbon printing, 237
 tissue, 238
Carbro process materials, 237
Carroll and Hubbard, 13, 16, 17, 72
Cartwright, H. M., 236
Cascade spreader, 149
Celluloid, 175
Cellulose acetate, 2, 175
 nitrate, 175
Characteristic curves, 204, 222
Charlesby, A., 129
Charrion and Vallette, 175
Chemicals, types of, 31
Chloride emulsions, 94, 99
Chloro-bromide, 94, 169
Chrome alum, use of, 28, 32
Clark, G. L., 128
Clark, W., 117
Clerc, L. P., 5, 19, 140, 238, 247
Cine base, tinted, 190
 negative emulsions, 187
 positive, 188
Coating machines, film, 176, 181,
 182, 184
 glass, 147
 paper, 162
 spreader, 148
Coating weight analyses, 231
Color contrast, 106
 formers, 125
 sensitiveness, 226
 sensitizers, 104
Contrast in emulsions, 99
Copper printing paper, 249
 salts, 249
Covering power, 166
Crocks, emulsion, 43
Cupric chloride, use of, 97

D

Daguerre, Louis Jacques Mandé, 1
Darkroom equipment, 42

illumination, 40
 layout, 38
 Davidson, L. F., 97
 Defender tripack, 119
 Densitometers, 210, 217, 220, 223
 Density range of emulsions, 19, 204
 Density, diffuse, 220
 parallel, 220
 Dewar flasks, 47, 216
 Diazotype printing, 249
 Dicyanin, 114, 116
 Dieterle and Reister, 116
 Diffraction grating device, 227
 Digesting pans, 47, 57
 Digestion of emulsions, 47, 73
 time of, 75
 vs speed, 74
 Dimitroff, G. Z., 215
 Dixon coating machinery, 162
 Duclaux and Janet, 135
 Dufaycolor film, 81, 82

E

Eder, J. M., x, 13, 66, 79, 107, 108, 212
 Eggert and Noddack, 231
 Ellis and Wells, 135
 Emulsions, bleach out, 251
 boiled, 6
 bromide paper, 166, 168, 169
 chloride, 3, 88, 94, 97, 98, 99, 170
 chloro-bromide, 94, 169
 cine negative, 68, 187
 cine positive, 63, 188
 collodion, 30, 199
 color-sensitive, 104
 comparative sensitivity, 103
 document, 79
 film pack, 117
 formulas, types of, 64
 infrared, 115
 keeping tests, 233
 lantern, 63, 89, 93
 Lippmann, 135
 mixed jet, 100, 188
 orthochromatic, 79, 105
 panchromatic, 105
 photogravure, 91
 positive, 188

process, 63, 89, 91
 reversal, 81, 83
 Schumann, 134
 self-filtering, 123
 shredding, 55
 silver phosphate, 200
 slow, Chapter V
 transparency, 3, 63, 93, 99, 102
 ultraviolet, 134
 X-ray, 132
 Engler viscometer, 24
 Eosin, 105, 112
 Erythrosin, 105, 107, 109, 112

F

Fabrics, sensitizing, 195, 242
 Feertype, 250
 Ferguson, W. B., 220
 Ferric compounds, sensitivity of, 242
 Ferroprussiate paper, 241
 Film base, acetate, 175
 nitrate, 175
 triacetate, 175
 Film, double coated, 121
 substratum, 178
 substratuming machines, 178
 triple coated, 125
 X-ray, 131
 Filtering, 50, 60
 Filters, light, 118, 121
 Finishing of emulsions, 73
 Fluorescent screens, 130, 133
 Fog, 173, 208
 Fog tests, 90, 234
 Fog-retarding compounds, 79
 Formula, structure of a, 64
 Friedman, J. S., 12

G

Gamma and grain size, 15
 and wavelength, 207
 infinity, 208
 time curves, 206
 Gaspar, Bela, 122
 Gelatin, characteristics of, 21, 30
 choice of, 22, 187
 sensitizing action of, 5

Gelatino-chloride emulsions, 2
 Glass substratum, 139
 washing of, 138
 Goldberg, 221
 Grain aggregates, 94
 photo-micrography of, 10, 18, 45
 Grain size and speed, 7, 15, 63, 83,
 86, 88
 Grain size *vs* gradation, 77
 Grain size *vs* time of precipitation,
 7
 Grain structure, 18
 Grinten, F. van der, 251
 Gum bichromate, 240

H

Halation, prevention of, 79, 93, 179
 Halides, combining proportions of,
 65
 Hardening of emulsions, 28
 Herzberg, W., 156
 Heyne, W., 68, 187
 Hubbard and Carroll, 13, 16, 17, 72
 Hurter and Driffield, 202, 208, 212
 Huzii, M., 21
 Hypersensitive emulsions, 254
 Hypersensitizing by bathing, 83,
 111, 253

I

Ice water, 54
 Illumination of darkrooms, 40
 Imbibition films, 190
 Inertia, 205
 regression of, 209
 Infrared sensitive emulsions, 115
 Intensifying screens, 130
 Iodides in emulsions, 12, 112
 Iron printing processes, 241
 Isocyanins, 112

J

Jahr, H., 77, 91, 96, 154
 Jones, Chapman, 97
 Jones, L. A., 225

K

Kallitype, 244
 Keeping of emulsion, 17, 50, 234
 tests, 233
 Kendall, J. P., 256
 Koebig, August, 52
 Koegel and Steigmann, 250
 Kopke, 24, 36
 Kryptocyanins, 116
 Kuhn, H., 121

L

Laboratory layout, 39, 53
 Lantern emulsions, 89
 Lea, M. Carey, 17
 Lehmann, 136
 Levelling tables, 143
 Levy and West, 133
 Levy, L. A., 132
 Lippmann emulsions, 135
 Lumière, A. and L., 81
 Lumière and Seyewetz, 236
 Luther, R., 257
 Lyman, T., 135

M

Maddox, R. L., ix, 2, 23
 Mannes and Godowsky, 122
 Materials for emulsion making, 33
 Mees, C. E. K., 111, 222
 Melting point determinations, 25
 Microscopy of grains, 10, 18, 45
 Mixed jet emulsions, 100
 Mixing of emulsions, 66, 77, 94
 Monopack emulsions, 121, 123
 Morgan and Lester, 205

N

Naphthol yellow, 106, 118, 120
 orange, 93
 Neocyanin, 116
 Nessler's reagent, use of, 72
 Nièpce de St. Victor, 22
 Nietz, A. H., 208
 Nitrate film base, 175
 Non-stress coating, 159
 Noodle press, 54, 55

O

Oakley, C. F., 80
 Opacity, 203
 Orthochromatic emulsions, 105
 Orthochrome, T., 110, 111, 114
 Ostwald ripening, 10, 66
 viscometer, 24
 Ozafilm, 250
 Ozalid process, 250

P

Packing materials, 153
 Palladiotype paper, 249
 Pans, digesting, 47
 Paper base, 156
 Pepper, 94, 174
 pH determinations, 232
 pH of emulsions, 72
 Phosphate emulsions, 200
 Photogravure emulsions, 88, 91
 Photometers, 212
 Photomicrography of grains, 18, 45
 Pinacyanol, 111, 123
 Pinaflavol, 109, 111, 112
 Pinaverdol, 110, 111
 Pizzighelli, J., 244
 Plate coating, 144
 Plate coating machines, 147, 150
 Plate testing, 215
 Platinotype paper, 246
 Ponton, Mungo, 23
 Printing-out papers, 196
 Process emulsions, 89
 Punnett, R. F., 5

R

Raw paper, 156
 Reciprocity law, 19
 Reeling machinery, 180
 Renwick, F. F., 107, 215, 225
 Resolution, 20, 87
 Resolving power, 20
 Reversal emulsions, 81, 84
 Rhodamin, 112
 Ripening, 10, 13

S

Safelights, 40
 Salted paper, 192
 Scheelite, 130
 Schinzel, K., 122, 124, 125
 Schumann emulsions, 134
 Schwarzschild factor, 19
 Sensitivity, cause of, 5, 253
 relative, 5
 Setting point, determination of, 27
 Shepherd, E. Sanger, 189, 220
 Sheppard, S. E., x, 2, 3, 5, 6, 10,
 23, 27, 256
 Sheppard and Houck, 2
 Sheppard and Mees, 212
 Shredder, hydraulic, 55
 Silver phosphate sensitizer, 200
 Smith, J. H., 6, 252
 Sodium sulphite sensitizer, 16
 Southworth, 7
 Spectral response, 103, 104, 106
 Spectrograph, construction of, 226
 Spreaders, 148
 Stabilizers, 256
 Staud and Connelly, 2
 Stelling, C., 24
 Step-wedges, 210, 230
 Sticky-back glass, 184
 Stirring apparatus, 101
 Storr, B. V., 23
 Strong, J., 19
 Stripping collodion, 30, 200
 Structure of a formula, 64
 Substratum for film base, 178
 for glass plates, 140
 Substratuming machines, 178
 Super-sensitization, 111
 Svedberg, The, 17

T

Tallent, A. K., 226
 Tartrazin, 106, 120
 Tetrocarbocyanin, 116
 Testing equipment, 210
 Thallium chloride, 171
 Thermometers, types of, 42
 Thermo-regulators, 58

Thermos flasks, 58
Thermostatic control, 57
Thiebaut, A., 249
Thiosinamin, 256
Thiourea, 256
Three layer coatings, 118, 122, 125,
191
Tien Kin, 134
Tissue, carbon, 238
Toy and Rawling, 223
Triacetate base, 175
Tripacks, 117
Trist, Ronald, 236
Trivelli, 3, 6
Trivelli and Shepard, 3
Trivelli and Smith, 6, 13, 14, 19, 74,
258
Truum, A., 199
Turbidity factor, 221

U

Ultraviolet absorption by gelatin,
134
Ultraviolet emulsions, 134
Unwashed emulsions, 169
Uranium process, 249

V

Valenta, E., 95, 96, 200
V-spreader, 148
Viscosimeters, 24
Viscosity of gelatin, 24
Visual spectral response, 103, 104,
106
Vogel, H. W., xi, 105
Von Weimarn, 8

W

Wall, E. J., 26, 66, 83, 91, 105, 168,
177
Warm tones, 94, 97
Washing glass, 138
Washing of emulsions, 48, 56, 70
Wash-Off Relief films, 189
Waterhouse, 105
Wavelength, scale, 229
Wedge photometer, 212
Wedges for sensitometry, 210
Weigert and Luhr, 64
Wellington, J. B. B., 95
Wiemarn, von, 8
Willis, W., 246
Wilsey and Pritchard, 129
Wivesleigh, de, W., x

X

Xenocyanin, 116
X-opaque gelatin, 132
X-ray intensifying screens, 130
emulsions, 115, 132

Y

Yellow, brilliant, 93, 106, 118
naphthol, 106, 118
thiazol, 106

Z

Zinc sulphide, 133
X-ray screens, 133