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E. A. WILLIFORD ET AL

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EMULSION SENSITOMETRY

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2 SHEETS—SHEET 1

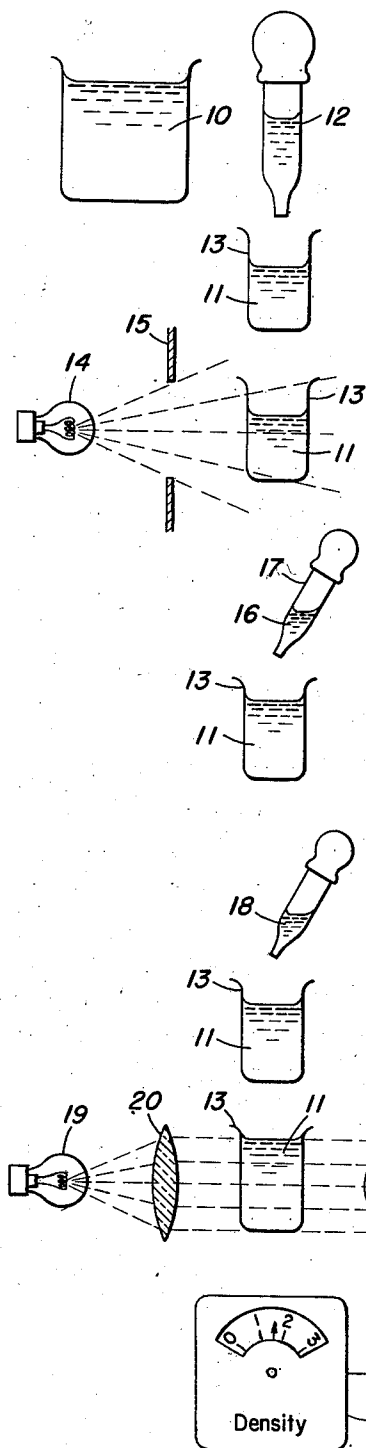
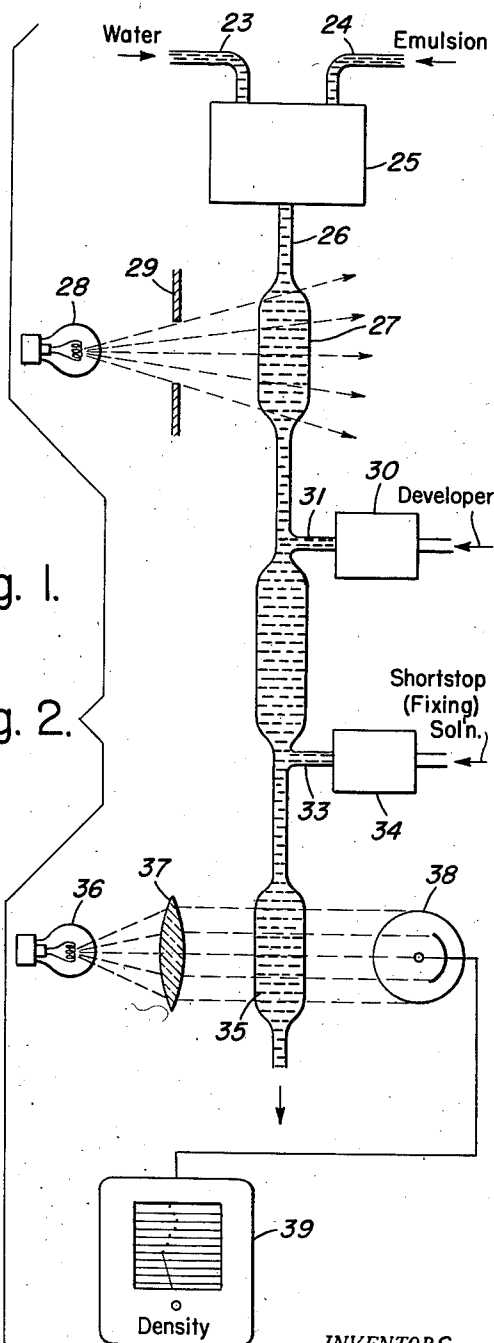


Fig. 1.

Fig. 2.



INVENTORS
Edward Allan Williford
Monroe H. Sweet
BY *Walter H. Kessel*
Walter H. Kessel
ATTORNEYS

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2 SHEETS—SHEET 2

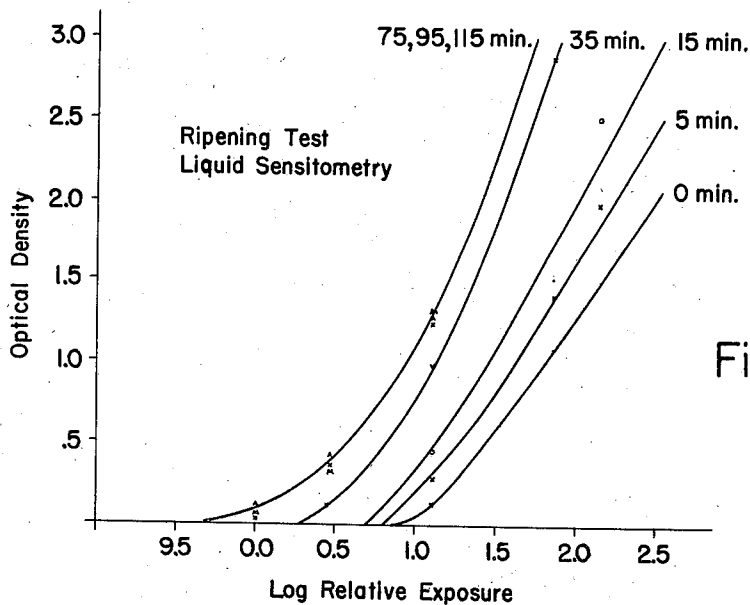


Fig. 3.

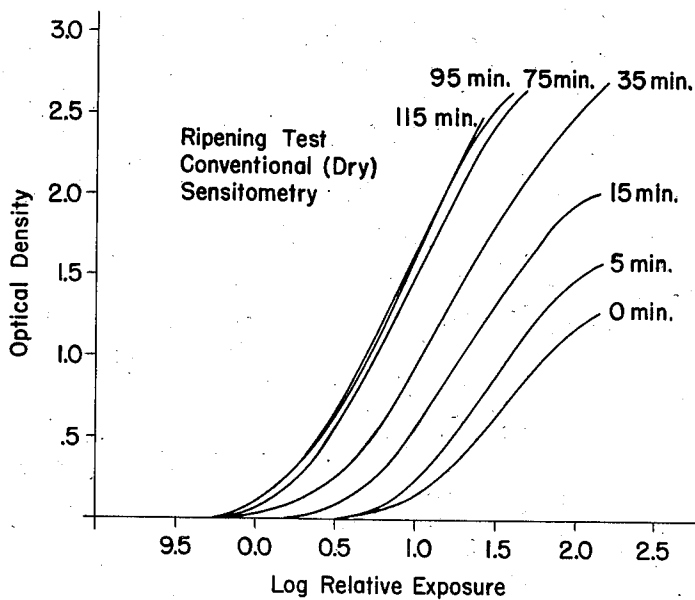


Fig. 4.

INVENTORS
Edward Allan Williford
Monroe H. Sweet

BY

Walter G. Sweet
Walter G. Sweet
ATTORNEYS

UNITED STATES PATENT OFFICE

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EMULSION SENSITOMETRY

Edward Allan Williford and Monroe H. Sweet,
Binghamton, N. Y., assignors to General Ani-
line & Film Corporation, New York, N. Y., a
corporation of Delaware

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10 Claims. (Cl. 23—230)

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This invention relates to an improved method for controlling and measuring the comparative light sensitivity and contrast characteristics of photographic emulsions, and for other measurements involving determination of densities produced on development of photographic emulsion coatings.

Photographic films and papers are ordinarily prepared by coating a suitable base, such as film, paper or other fabric, with a photographic emulsion, particularly of the type containing a light-sensitive silver halide suspended in gelatin or other viscous protective colloid, and allowing the coating to dry on the base. The emulsion is generally prepared in batches, and since the photographic characteristics of the resulting coatings are sensitive to numerous variables in the course of manufacture, it is customary to test each batch before applying it to a base, e. g., in order to insure that uniform quality will be maintained. Heretofore, the testing method employed approximated the intended use of the emulsion. Thus in carrying out the test, a sample of the emulsion was coated on a sheet of backing material, and dried thereon. The resulting sensitized material was cut into strips, exposed to light of graduated intensity, developed, washed and dried, and then subjected to measurement of the opacity or density of the resulting image in a densitometer. From the data thus obtained, various photographic characteristics of the material can be determined. Thus, by plotting density against log exposure, a curve is obtained showing the gradation and sensitivity of the emulsion coating. Such tests are relatively time consuming, requiring hours or even days, and in the meantime, substantial portions of equipment are required to store the batch of emulsion, contributing substantially to overhead costs.

It is an object of this invention to provide a rapid and simple method for determining relative densities produced upon exposure and development of a photographic emulsion, and hence, such properties as the relative speed and contrast characteristics of the resulting sensitized material, with a high degree of accuracy, said method requiring relatively simple and economical equipment which can be readily operated without unusual skill, and which is adaptable for a wide range of conditions of use.

We have discovered that samples of photographic emulsions of the type employed in making light sensitive layers by coating and drying processes, particularly emulsions containing a

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light-sensitive silver halide such as silver bromide suspended in an aqueous gel forming colloid such as aqueous gelatin, exposed in liquid form to light, and reduced in a standardized manner with a photographic developer, are darkened to an extent which can be accurately measured by determining the optical density of a layer of standard thickness of the developed sample; and that these measurements bear substantially the same inter-relationship as measurements obtained in the customary manner, described above, wherein a sample of the emulsion is coated on a sheet, dried, and test strips prepared therefrom by conventional exposure and development, and density measurements made from the test strips.

Thus, in accordance with one embodiment of the invention, comparative speed and gradation obtainable in coated materials prepared with a batch of silver halide-gelatin emulsion are determined as follows: a sample of the liquid emulsion, as such, or if desired, diluted with a predetermined proportion of water, is divided into equal portions which are placed in a number of containers of standard shape and size, which are transparent to light of the type which it is desired to test for exposure of the emulsion. The samples are then irradiated respectively with graduated amounts of light, e. g., by using constant intensity and different periods of exposure, or a fixed period with illumination of graded intensity. A measured quantity of developer solution is then added to each of the irradiated samples, and after development for a predetermined period, the action is arrested by addition of a measured quantity of a short stop or fixing solution. Thereupon, the density of the resulting coloration or opacity of the samples to transmitted light is measured by conventional densitometer means. A curve or series of curves in which density is plotted against log exposure, obtained from the results of measurements made in this process, we have found, accurately represent the relative characteristics of the emulsion in the same way as a curve or curves obtained by the conventional testing method. However, instead of requiring hours or days, the measurements in the test of this invention are completed in a matter of minutes, thus permitting further processing and use of the emulsion without substantial delay, and appreciably reducing the overhead expense involved.

A convenient method of carrying out the testing procedure of this invention involves placing

a series of samples of an emulsion on a moving belt or conveyor, and advancing the samples progressively to successive stations at which dilution (if employed), exposure, development, addition of fixing or short stop solution, and measurement of density are respectively carried out. If desired, these operations can be made automatically, or they can be carried out by hand. The emulsion samples are shielded from light during all operations, except for the controlled irradiation, until development is complete.

Moreover, if it is desired to maintain continuous control of the sensitivity or gradation of an emulsion, the successive steps of the present test can be carried out in a stream of emulsion flowing at a predetermined rate in a tube or conduit, dilution, exposure, development, fixing or short stop, and measurement of density taking place by operations, or addition of reagents at a suitable rate, at successive points in the flowing stream, measurement of density being carried out at a final point and the results of said measurement being continuously recorded if desired.

The various steps in the process of the invention will be more fully understood from the accompanying drawings which illustrate the procedure and the results obtained thereby. In the drawings,

Figure 1 is a schematic view showing a sample of emulsion in successive stages of the testing procedure.

Figure 2 similarly represents an arrangement for carrying out the procedure of the invention in a continuous manner.

Figure 3 is a series of density-log exposure curves obtained in testing a typical silver bromide emulsion at various stages of ripening, in accordance with the present invention.

Figure 4 is a series of curves prepared with the same emulsion as in Figure 3, in a parallel series of tests, employing the conventional method of testing.

Referring to Figure 1, a quantity of photographic emulsion, e. g., a silver bromide-gelatin emulsion, is melted and thoroughly mixed with water to form the test mixture 10. A dilution ratio can be chosen so as to yield a density or opacity, in the apparatus employed in the final step of the test hereinafter described, within the measuring range of the densitometer. For example, in testing one ordinary emulsion, dilution of 1 part by volume thereof with 30 parts by volume of water was found satisfactory. A standard sample 11, e. g., about 20 cc. of the resulting solution, measured for example in a pipette 12, is placed in a cuvette 13 or similar vessel, of a material which is transparent to light of the wavelength to be employed in the ensuing exposure. The cuvette may be one having for example a capacity of 30 cc. and a thickness of 1 centimeter.

The sample 11 is irradiated uniformly in cuvette 13 with a measured quantity of light, e. g., obtained from light source 14 and controlled by a suitable intensity control device 15. The latter may include for example a neutral density wedge for controlling intensity, an iris diaphragm, or the like. The exposure is timed to yield the desired quantity of irradiation. For example, in the case of a silver bromide-gelatin emulsion of medium sensitivity, an exposure of the order of two meter-candle-seconds is sufficient to produce darkening. If it is desired to test the sensitivity of the emulsion to light of

predetermined spectral quality, an appropriate light source can be used for producing the desired wavelength, and if necessary, color filters can be interposed between the light source 14 and the cuvette 13 containing sample 11.

When exposure is complete, development is effected by adding a measured quantity (e. g., 5 cc.) of a developer solution 16 to the sample 11 in cuvette 13 and thoroughly agitating the resulting mixture. By employing a syringe 17 for addition of the developer, sufficient force can be imparted to the stream of liquid to produce adequate mixing without additional agitation. The developer is allowed to react with the irradiated sample for a predetermined period; for example, from 3 to 6 minutes has been found satisfactory for a normal developer. Such a developer may contain, for example, the following ingredients in sufficient water to yield 1 liter of solution:

p-Methylamino phenol -----g--	2
Na ₂ SO ₃ -----g--	100
Hydroquinone -----g--	5
Borax -----g--	2

To arrest development at the end of the desired period, a reagent 18 is added which may be, for example, 1 cc. of 2% acetic acid or 2 cc. of acid fixing solution such as an aqueous solution containing 12% sodium thiosulfate and 1% acetic acid.

The optical density of sample 11 is then measured in a densitometer, shown as comprising a light source 19, a collimator 20 and a photoelectric cell 21 receiving illumination from the collimator through sample 11, and registering the relative density of the latter on the meter 22.

A succession of cuvettes such as that shown in Figure 1 can be advanced in a series on a conveyor or belt, and the various operations described above can be carried out at successive stations along the belt, i. e., automatically or by hand.

A different form of apparatus for the process of this invention is shown in Figure 2. In this case, the water for dilution and the melted silver halide-gelatin emulsion are brought through conduits 23 and 24 into a proportioning device 25 in which they are thoroughly mixed and wherein the relative amounts to yield the desired concentration are measured.

The diluted emulsion passes thence through a main flow tube 26 at a constant predetermined rate of flow, and is subjected to uniform irradiation of desired intensity in an exposure zone 27, the illumination being derived from light source 28 and controlled by a device 29 of the same type as the device 15 described hereinbefore. Beyond the exposure zone 27, a developer solution is introduced into the flowing stream at a constant rate maintained by a regulating device 30, through a side tube 31 into the main flow tube 26.

Development occurs in the succeeding developing zone 32 which is made of sufficient length and cross-section to afford the requisite period of development for the flow rate of the stream. To arrest development, a suitable solution such as dilute acetic acid, or an acidified sodium thiosulfate solution, is introduced into the tube 26 through a side tube 33 joining the tube 26 at the end of development zone 32, the solution added at this point being introduced at a constant rate by means of the proportioning device 34.

Beyond the junction of inlet tube 33, tube 26 conducts the developed emulsion through a den-

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sity measuring zone 35 in which a beam of light from a source 36 passes through collimator 37 and thence through the stream of emulsion in zone 35 to a photocell 38 of which the output controls a recording densitometer 39. A continuous record can thus be maintained of the speed or density characters of the emulsion for predetermined exposure.

It is noted, when a fixing agent such as sodium thiosulfate is used to arrest development, the opacity of the suspension to be measured is practically entirely due to the developed silver; while if only an acid such as acetic acid is used, then part of the opacity is caused by undeveloped silver halide, and a corresponding correction should be made in order to determine absolute values for the sensitivity measurements.

Typical curves obtained in the procedure of Figure 1 are shown in Figure 3. These curves were determined from a series of samples taken from the same batch of silver bromide-gelatin emulsion at various intervals during the ripening period, and as indicated by the time in minutes shown in the drawing, the curves represent the density versus log exposure of the unripened emulsion and of the same emulsion after ripening for 5, 15, 35, 75, 95 and 115 minutes. For purposes of comparison, a parallel series of tests was made by coating sheets of paper with the same emulsion at the same time intervals during the ripening treatment, drying, exposing to graded quantities of illumination, measuring the resulting densities, and plotting the results in terms of optical density versus log relative exposure. The resulting curves are shown in Figure 4. A comparison of the two sets of curves clearly indicates that the slope and relative location of the curves determined in accordance with the method of this invention yield the gradation and speed characteristics or inertia in the same manner as curves obtained in the conventional testing procedure, and give the same indication of completion of ripening.

Similar results have been obtained employing the procedures and apparatus hereinbefore described, but omitting the initial dilution of the emulsion sample with water. Instead, the emulsion, in liquid form, is introduced directly into the testing equipment, exposed in the form of measured samples or at a predetermined flow rate, in a layer of suitable standard depth to be translucent, to controlled quantities of light; and after development in a standardized manner, as described above, the emulsion sample or samples are measured for density in a layer having a depth adapted to the range of the densitometer employed. In many cases, omission of the initial dilution step provides even more accurate or reliable results than when dilution is used.

The testing procedure of this invention can be applied to other types of emulsions than silver bromide-gelatin emulsions, including those containing other suspended light sensitive silver halides and viscous colloidal suspension media other than aqueous gelatin, e. g., albumen, natural and artificial resins and gums, organic derivatives of cellulose, and the like. When the suspension medium is not compatible with water, other solvents such as alcohol, acetone, or mixtures thereof with water or with each other can be used for addition of developer, short-stop and fixing reagents, and for dilution, so as to preserve the colloidal nature of the mixture during the test. Additional materials modifying the properties of the emulsions, such as sensitizing

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dyestuffs, color formers for color photography and the like can also be present in the emulsion during a test in accordance with the invention.

Emulsions for use in color photography can also be advantageously tested according to the process of this invention. Such emulsions contain, for example, a color former which reacts with the oxidation products of the developer, produced upon reaction with light-exposed silver halide, to form a dye. For example, the color formers can be naphthols, pyrazolones or acyl-acetariylides yielding respectively cyan, magenta or yellow dyes with oxidation products of a color-forming developer such as p-amino-diethylaniline. Emulsions containing a cyan color former are sensitized to red light, and those containing a magenta color former are sensitized to green, while a yellow color former is generally employed with a color-blind or blue-sensitive silver halide emulsion.

In testing such emulsions in accordance with the present invention, the light from source 14 or 28 of Fig. 1 or 2 for exposing the test emulsion can be advantageously of the color to which the emulsion is sensitive, or in special cases, of another color for which it is desired to test the sensitivity of the emulsion. The developer added at the next stage is chosen to yield a color with the color former. After addition of the short-stop, a reagent is added which converts the silver to silver halide, e. g., a ferricyanide and sodium chloride solution. A fixing agent can also be added to dissolve the silver halide. There is formed thereby a sample containing the developed color in a concentration corresponding to the sensitivity of the emulsion. The light from source 19 or 36 is chosen or filtered to have its principal wavelength corresponding to maximum absorption of the color produced. Accordingly, the intensity of illumination reaching the photocell 21 or 38 and indicated or recorded by meter 22 or 39 is a measurement of the color density produced in the emulsion, yielding data from which sensitometric curves can be plotted in the same manner as hereinabove described.

The present testing procedure can be utilized to follow the ripening of a batch of emulsion, to compare the speed and contrast of different emulsions, to compare the development obtained under various conditions of time, temperature, concentration and composition, and for other tests wherein comparative densities were previously determined by making test strips from the emulsion and developing and measuring the same in the conventional manner.

Variations and modifications can be made in this invention without departing from the scope or nature thereof, and portions thereof can be used without others.

We claim:

1. A process for measuring the sensitometric characteristics of a photographic silver halide emulsion which comprises exposing a test portion of the emulsion in liquid form to a predetermined quantity of illumination, developing the exposed test portion while liquid, and determining the optical density of the developed liquid test portion to transmitted light.

2. A process according to claim 1 wherein a predetermined proportion of a diluent is added to the original emulsion to form said liquid test portion.

3. A process according to claim 1 wherein light of predetermined spectral quality is employed in exposing said liquid test portion.

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4. A process for measuring gradation and speed characteristics of a photographic silver halide emulsion which comprises exposing a series of test portions of the emulsion in liquid form respectively to graded quantities of illumination, developing the exposed test portions while liquid under similar conditions, and determining the optical densities of the developed liquid test portions to transmitted light.

5. A process for measuring the relative sensitometric characteristics of an aqueous photographic silver halide emulsion which comprises exposing a test portion of the emulsion in liquid form to a predetermined quantity of illumination, developing the exposed test portion while liquid, arresting development thereof at the end of a predetermined period, and determining the optical density of the developed liquid test portion to transmitted light.

6. A process as defined in claim 5 wherein a fixing agent is added to the developed liquid test portion prior to determination of the optical density, so as to dissolve the silver halides therein.

7. A process for measuring the relative sensitometric characteristics of a photographic silver halide emulsion which comprises placing a sample of the emulsion in liquid form in a transparent container, exposing the sample in the container to a predetermined quantity of illumination, adding a predetermined quantity of developer solution to the sample in the container, and after a predetermined developing period, adding a predetermined quantity of short stop solution thereto, and measuring the opacity of the developed composition in the container to transmitted light.

8. A process as defined in claim 7 wherein the short stop solution includes a fixing agent for dissolving the silver halides in the sample.

9. A continuous process for measuring the relative sensitometric characteristics of a photographic silver halide emulsion which comprises

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causing a portion of the emulsion in liquid form to flow in a stream at a predetermined constant rate, exposing a limited zone of said stream to illumination of predetermined intensity, adding a developer at a constant rate to said stream beyond the exposure zone, adding a development arresting reagent at a constant rate at a point spaced from the point of introduction of said developer, the intervening portion of the stream constituting a development zone, and measuring the optical density of the stream to transmitted light beyond said development zone.

10. A process for measuring the relative sensitometric characteristics of a color-forming photographic silver halide emulsion which comprises adjusting the concentration of a fluid sample of the emulsion to a predetermined value, exposing a test portion of the resulting composition in fluid form to a predetermined quantity of illumination having a color to which the emulsion is sensitive, color-developing the exposed test portion and bleaching the silver thus produced, and determining the optical density of the developed test portion to transmitted light of a principal wavelength corresponding to maximum absorption of the color produced in the test portion.

EDWARD ALLAN WILLIFORD.
MONROE HAMILTON SWEET.

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