April 3, 1956 J. WARREN 2,740,713

SENSITIZATION OF PHOTOGRAPHIC EMULSIONS

Filed April 26, 1952 2 Sheets-Sheet 1

FIG. 1.

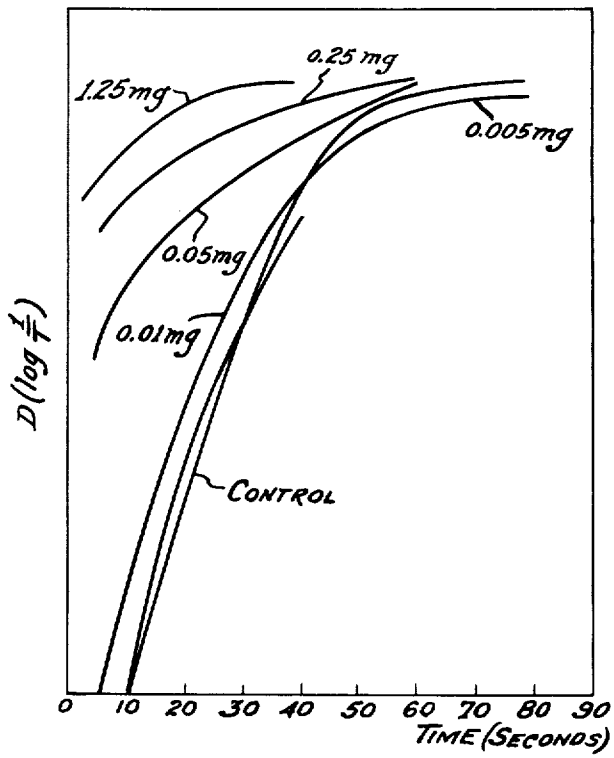
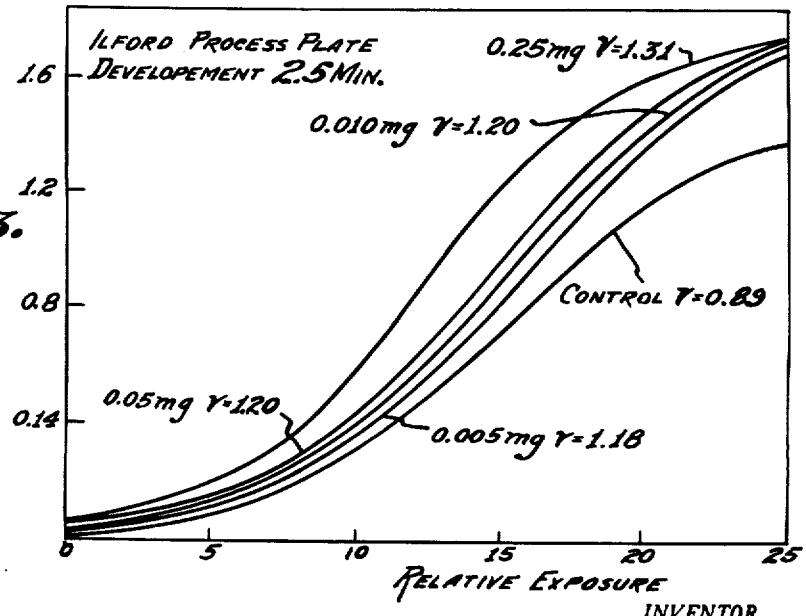


FIG. 3.



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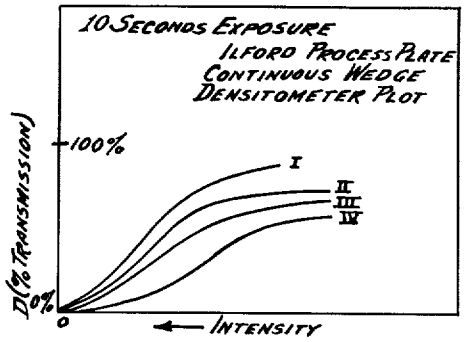


FIG. 2a.

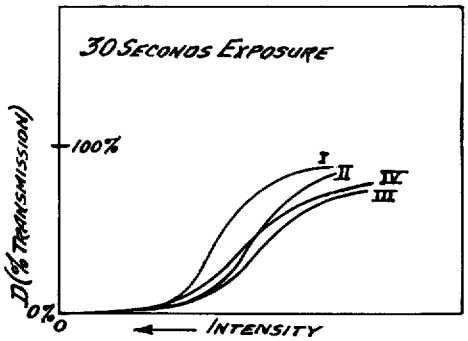


FIG. 2b.

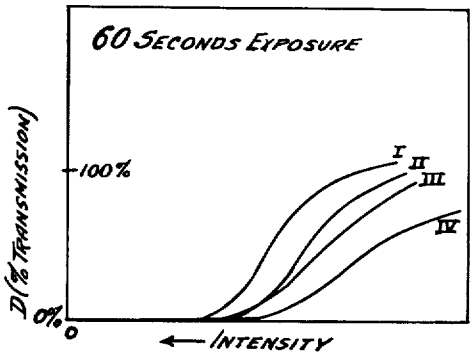


FIG. 2c.

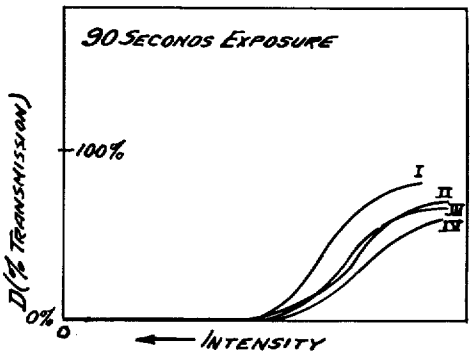


FIG. 2d.

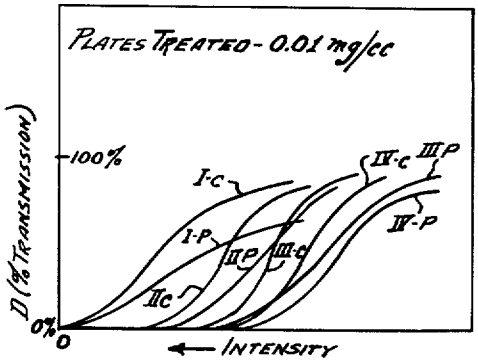


FIG. 2e.

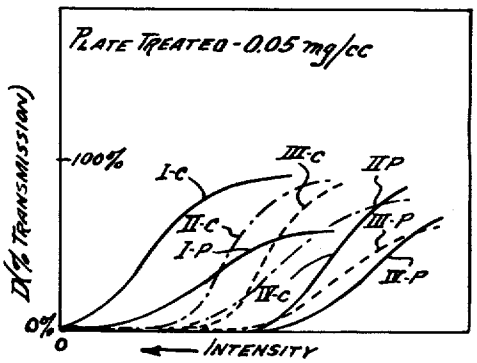


FIG. 2f.

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SENSITIZATION OF PHOTOGRAPHIC EMULSIONS

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Application April 26, 1952, Serial No. 284,506

17 Claims. (Cl. 95—7)

This invention relates to the sensitization of photographic emulsions and to the modification of certain of their properties.

The sensitization of silver halide emulsions is known. There are a number of chemical agents by means of which the speed and usually the gamma of the emulsion may be increased.

It is an object of the present invention to provide a method for accelerating the rate of development of exposed silver halide-gelatin emulsion. Another object is to provide a developer containing a sensitizing agent whereby the state of development is accelerated. Yet another object of the invention is the provision of an emulsion containing a sensitizing agent. Still another object of the invention involves the provision of an agent which may be applied to an ordinary emulsion at any time prior to fixation which will increase the sensitivity and rate of development, as well as the gamma of the emulsion.

These and other objects of the invention which will be pointed out in greater detail hereinafter, or which will be apparent to one skilled in the art upon reading these specifications, I accomplish by that series of method steps and by that developer, and by that emulsion, of which I shall now disclose certain exemplary embodiments.

Reference is made to the drawings forming a part hereof, and in which:

Figure 1 is a graph showing the effect of an addition of the invention to a developer of the rate of development;

Figures 2A to 2F inclusive are graphs showing the effect of treating an emulsion prior to exposure on the sensitivity;

Figure 3 shows the effect of development of ordinary emulsions in developers containing an agent according to my invention.

I have found that protamines (a class of strongly basic proteins of low molecular weight) have an extraordinary sensitizing effect on silver halide emulsions. The protamines are a class of highly basic, water soluble compounds found in nature in combination with nucleic acids, and they are derived commercially from the sperm of several species of fish. The structural formula of protamines is unknown. They have an isoelectric point in the region of 12.0 and combine with a large number of other proteins to form complexes whose solubility is related to the salt concentration. One of these protamines, i. e., salmine, which is the protamine derived from the salmon, according to available data contains seven amino acids and has a molecular weight of about 8000. While all of the protamines appear to have the qualities necessary according to the present invention, I have found extremely suitable the protamines derived from the salmon (salmine) or from the herring (clupein).

I have found that contact with a protamine solution not only accelerates development, but also increases the density for a given exposure. This acceleration in development and this intensification may be demonstrated at all wave lengths which will produce a latent image on a photographic emulsion. I have found that images resulting from exposure to X-rays, electrons, visible and infrared sources are affected by the protamines.

I have determined that the accelerated development rate and increase in density can be obtained in a number of ways. The protamine may be added to the emulsion prior to the deposition of the emulsion on the plate. The protamine may be applied to a plate carrying on emulsion either by dipping or by means of a spray. The application of the protamine in this way to the plate may be carried out prior to exposure, or after exposure and before development, or after development and before fixing, and in all cases the density of the plate is enhanced and the development rate is accelerated. Furthermore, I have found that the protamine may be added to the developer, and a plate having a conventional emulsion and having no protamine treatment prior to development will display the results above outlined if the developing solution contains the protamine.

I have found also that the action of protamines on an emulsion occurs over a wide range of pH. When plates were immersed in protamine solutions buffered from pH 4.6 to pH 8.8 the activity was continued. The reaction of the protamines with photographic emulsion is very rapid and the effect is not apparently enhanced by an increase in the contact time beyond a few seconds.

While the protamine may be applied in many forms I prefer to apply it in the form of the sulfate salt.

The following examples will be illustrative of the procedures which may be followed and of the results which will be accomplished.

Example 1:—25 Ilford process plates were placed on a tray and simultaneously exposed for two seconds to an incandescent lamp. These 25 plates were divided into six groups of four plates each.

The four plates of the six groups were developed in standard methol-hydroquinone developer containing respectively no protamine sulfate, 0.005 mg./cc., 0.01 mg./cc., 0.05 mg./cc., 0.25 mg./cc., and 1.25 mg./cc. of protamine sulfate

The four plates which were developed in the standard developer without protamine sulfate were developed respectively for 20, 40, 80 and 160 seconds. The four plates of the remaining groups which were developed in the developer containing protamine sulfate were developed respectively for 5, 10, 20 and 40 seconds with agitation, except that in the case of the solution containing 1.25 mg./cc. of protamine sulfate an additional interval of 2.5 seconds was tested.

In each case the developer temperature was 17.8 to 18.4° C. Each plate was plunged into an acid stop bath and hypo as rapidly as possible after development. The densities of these plates in relation to the time of development are plotted in Figure 1.

Under the above outlined conditions the latent period of an untreated plate was about 25 seconds and densities in the region of 1.5 were reached in approximately 75 seconds. When the developer contained protamine the rate of development was increased roughly in proportion to the amount of protamine added. With 0.01 mg./cc., the toe of the normal curve was lost and the time-density

relation is practically a straight line relation. An increase in the concentration of protamine continues to accelerate development so that with 1.25 mg./cc. a density of 2.0 was reached in 30 seconds. Substantially instantaneous development occurs at concentrations of 2.0 mg./cc. or more.

The developer referred to above as the "standard metol-hydroquinone" comprises two solutions as follows:

Solution A

Pot. bromide	gm..	12.0
Hydroquinone	gm..	20.0
Pot. metabisulfite	gm..	20.0
Water q. s	cc..	1000.0

Solution B

Sodium hydroxide	gm..	40.0
Water q. s	cc..	1000.0

Equal parts of A and B and water are mixed just before use. In the above examples conventional fixation and washing was employed.

Example 2.—The following protamine solutions were prepared in a phosphate buffer of pH 7.6, and having concentrations of 0.2 mg./cc., 0.05 mg./cc., 0.01 mg./cc., 0.005 mg./cc. and none. Four groups of Ilford process plates were half immersed for 30 seconds, one in each solution. After drying in darkness, the plates were covered with an Eder-Hecht continuous wedge (wedge constant 0.401, relative sensitivity 122.2) and exposed to an incandescent light. The plates which had been immersed in each of the solutions were exposed respectively for 10, 30, 60 and 90 seconds, and then all were developed for two and one-half minutes in a standard metol-hydroquinone developer,

Group	Protamine Concentration, mg./cc.	Exposure Time, seconds	Development Time, minutes
IV	0.20	10	2.5
	0.20	30	2.5
	0.20	60	2.5
	0.20	90	2.5
III	0.05	10	2.5
	0.05	30	2.5
	0.05	60	2.5
	0.05	90	2.5
II	0.01	10	2.5
	0.01	30	2.5
	0.01	60	2.5
	0.01	90	2.5
I	None	10	2.5
	None	30	2.5
	None	60	2.5
	None	90	2.5

The density curve for each half of the plate was recorded on a microphotometer and the results are plotted in Figure 2.

From this figure it will be observed that the density of the protamine-treated emulsion always exceeds that of the control half for the exposures tested. Similarly, the gamma of the treated plates is greater for any given exposure.

Example 3.—Five groups of five Ilford process plates each were exposed for periods of 1.0, 0.5, 0.2, 0.1 and 0.04 second to an incandescent source. One plate of each exposure was developed for two and one-half minutes in standard hydroquinone developer containing respectively no protamine, 0.25 mg./cc., 0.05 mg./cc., 0.01 mg./cc. and 0.005 mg./cc. The plate densities are plotted in Figure 3.

It will be noted that concentrations between 0.005 mg./cc. and 0.05 mg./cc. result in essentially similar gamma values as compared with the control. With 0.250 mg./cc. the gamma was 1.3, but the density at two and one-half minutes was essentially the same for all the

protamine-developer group. Fogging was encountered with the 0.25 mg./cc. and 0.05 mg./cc. concentration and this amounted to 12% and 10% respectively of the density for these developers. Hence, these particular curves in Figure 3 have been corrected for background according to the method of Pierce and Nachtreib (Ind. Eng. Chem., Anal. Ed. 13,774, 1941).

It will be understood that throughout the specification and claims where I have used the word "plate" I intend to cover the medium upon which the emulsion is carried, whether it be glass or a film of acetate or the like.

Furthermore, as pointed out above the method can be carried out in a number of ways, and I therefore do not intend from the method aspect to limit myself to any particular protamine.

It will be understood that modifications may be made without departing from the spirit of the invention, and I therefore do not intend to limit myself except as set forth in the claims which follow.

Having now fully described my invention what I claim as new and desire to secure by Letters Patent, is:

1. A light sensitive silver halide photographic emulsion, containing a protamine as a sensitizing and accelerating agent.

2. A light sensitive silver halide photographic emulsion, containing a protamine sulfate as a sensitizing and accelerating agent.

3. A light sensitive silver halide photographic emulsion, containing salmine as a sensitizing and accelerating agent.

4. A light sensitive silver halide photographic emulsion, containing clupein as a sensitizing and accelerating agent.

5. A photographic plate bearing a light sensitive silver halide photographic emulsion, said emulsion having a coating thereon of clupein serving as a sensitizing and accelerating agent.

6. In the method of making a sensitized photographic plate wherein a silver halide emulsion is deposited on a plate, the step of adding a protamine to said silver halide emulsion before its deposition on said plate.

7. A metol hydroquinone developer for photographic emulsions containing a protamine as a sensitizing and accelerating agent.

8. A metol hydroquinone developer for photographic emulsions, containing a protamine sulfate as a sensitizing and accelerating agent.

9. A metol hydroquinone developer for photographic emulsions containing as a sensitizing and accelerating agent a protamine selected from the class consisting of salmine and clupein.

10. A photographic plate bearing a light sensitive silver halide photographic emulsion, said emulsion having a coating thereon of a protamine, serving as a sensitizing and accelerating agent.

11. A photographic plate bearing a light sensitive silver halide photographic emulsion, said emulsion having a coating thereon of a protamine sulfate serving as a sensitizing and accelerating agent.

12. A photographic plate bearing a light sensitive silver halide photographic emulsion, said emulsion having a coating thereon of salmine serving as a sensitizing and accelerating agent.

13. The method of increasing the development speed of a photographic plate having a silver halide emulsion which has been exposed, which includes the steps of developing it in a metol hydroquinone developer to which there has been added a protamine, and fixing it in a conventional hypo fixing solution.

14. In a process of exposure, development and fixation of a silver halide photographic emulsion, the step of coating said emulsion with a protamine solution before said exposure.

15. In a process of exposure, development and fixation of a silver halide photographic emulsion, the step of coating said emulsion with protamine solution before said fixation.

16. In a process of exposure, development and fixation of a silver halide photographic emulsion, the step of coating said emulsion with a protamine solution after said exposure and before said development.

17. In a process of exposure, development and fixation of a silver halide photographic emulsion, the step of coating said emulsion with a protamine solution after said development and before said fixation.

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