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DRY HYPERSENSITIZING OF PHOTOGRAPHIC EMULSIONS

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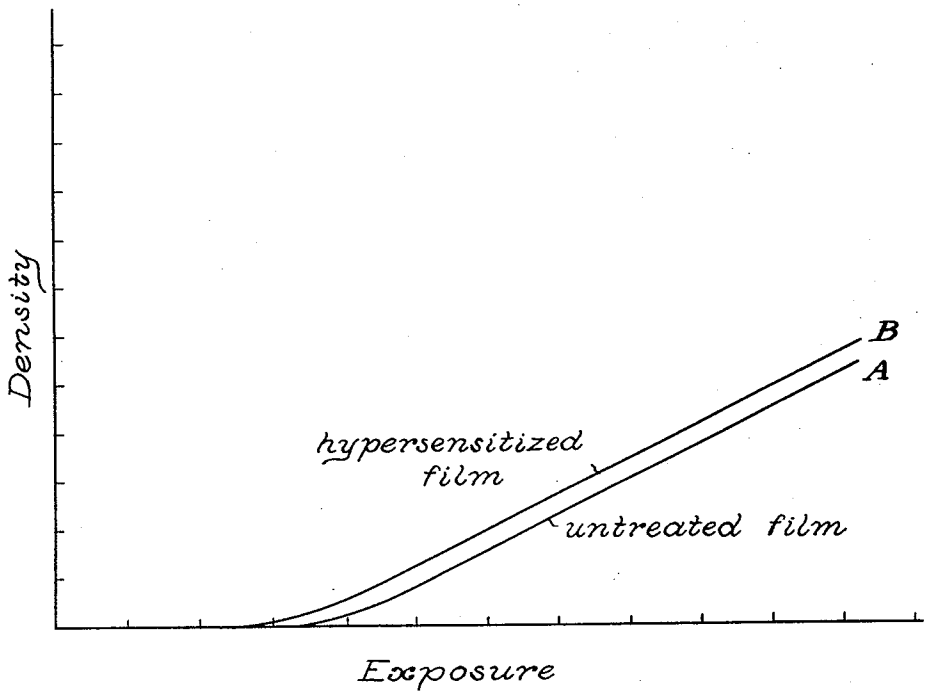

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DRY HYPERSENSITIZING OF PHOTOGRAPHIC EMULSIONS

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6 Claims. (Cl. 95—7)

The present invention relates to the hypersensitizing of photographic emulsions. Many methods for hypersensitizing photographic materials are known. In most all of these methods bathing of the photographic material in aqueous solutions of certain chemicals, for instance silver nitrate or ammonia, or silver nitrate and ammonia, is necessary. These bathing methods, which may be called wet hypersensitizing methods, however, in most cases injure the stability of the photographic material. Another disadvantage of this special treatment is that great care must be observed in manipulating the wet film. Careful re-drying of the emulsion is of utmost importance to the success of the procedure. Moreover, for some purposes the wet hypersensitizing methods are not practical for the reason that they increase the sensitivity of panchromatic emulsions in the yellowish-green and red sensitive portions more than in the blue. This means that the filter factors of the wet hypersensitized emulsion are different from those of the original emulsion which in turn means an increase in gamma of the wet hypersensitized panchromatic emulsion.

H. H. Duerr and myself have recommended a method (paper presented at the fall meeting of the S. M. P. E. in 1936) for the "dry hypersensitizing" of photographic emulsions which has many advantages over the "wet hypersensitizing" methods. This method involves the discovery that photographic material, when kept in contact with mercury vapor at room temperature for a certain length of time, shows an increase in photographic sensitivity to light of wave lengths to which the emulsion was originally sensitive.

Now it is generally known that mercury is a very dangerous substance to work with. In order to overcome the hazards met in working with mercury, efforts have been made to discover a material which could be employed in lieu of mercury while at the same time obtaining the hypersensitizing effect which can be obtained by the use of mercury. It is the object and purpose of the present invention to provide for the hypersensitizing of photographic emulsions by means of a substance which permits of the dry hypersensitizing of the emulsions and at the same time is free from the disadvantages incidental to the employment of mercury for this purpose.

It has been found that the dry hypersensitizing of photographic emulsions may be effected by the utilization of amalgams and that at the same time the dangers which arise when mercury is so used are completely avoided. While any amalgam is effective in attaining the desired end, for best results I prefer the amalgams of silver, copper, tin and zinc. Most of the amalgams, for instance those mentioned above, are powders and therefore are much more amenable to handling than mercury, especially in the hypersensitizing of photographic materials. Again, most amalgams are harmless substances when compared with mercury. In this connection attention may be directed to the customary use of amalgams as fillings for dental purposes. It is indeed surprising that these amalgams, although they emit only very slight traces of mercury vapor (otherwise manifestly they could not be used as fillings for dental purposes) show a distinct hypersensitizing effect on photographic emulsions.

The increase in speed can be obtained by bringing an emulsion either during its preparation or when in the form of a photographic film—the film being either wrapped or unwrapped—either into direct contact with an amalgam or in proximity thereto. The emulsion may be submitted to the action of the amalgam at room temperature or at a slightly elevated temperature, that is at an elevated temperature below that at which the film will be injured. If the hypersensitizing is effected at room temperature, a good effect is obtained in 2 to 3 days' time whereas, if the hypersensitizing be carried out at an elevated temperature, a shorter time suffices.

The hypersensitizing effect of the amalgams can also be obtained when photographic films or plates, which have already been exposed, are submitted to the action thereof. In other words, it is possible to intensify the latent image after exposure but prior to developing. It has been found that in this case the effect of the amalgam is even greater than it is on the unexposed emulsion. The treatment of the exposed film with the amalgam can be handled in exactly the same way as the treatment of the unexposed film. By this method it is possible, for instance, to correct an underexposed picture by treating the film for a suitable length of time, provided of course it is known or suspected beforehand that the film is underexposed.

The invention is further illustrated by the accompanying self-explanatory drawing in which curve A represents the density of a non-hypersensitized material, and curve B represents the density of the same material which has, however, been hypersensitized according to the method of the present invention.

The invention is further illustrated by the fol-

lowing examples, although it is to be understood that the invention is not restricted thereto.

Example 1.—A small amount, i. e. about one tenth to one half gram of silver amalgamate (20–80% mercury) is spread on the bottom of a container which is capable of being closed by a cover. The amalgamate, which is a powder, may be covered with a piece of paper or may be placed in a paper envelope. Photographic material, either wrapped or unwrapped, is maintained in this container for a period of from 12 hours to 8 days. After that time the sensitivity of the photographic emulsion has increased from 50 to 120%.

Example 2.—Photographic material, for example a roll film or a Leica spool, is taken out of the wrappings as would be done for daylight-loading. About 100 mg. of amalgamate are then placed between the spool (which is still lightproof) and the outside wrapping (foil paper). After 1 to 8 days it will be found that the sensitivity of the material has increased from 50 to 120%.

Example 3.—100 to 250 mg. of silver amalgam are placed in a paper envelope and the envelope brought into contact with any kind of photographic material for a period of from about 3 to 8 days. The sensitivity of the material is thereby greatly augmented.

Example 4.—A paste consisting of silver amalgam and glue is coated on a sheet of paper and dried. The paper so obtained is brought into contact with wrapped or unwrapped photographic film for a period not exceeding 8 days.

Example 5.—A roll film which has been exposed in a camera and re-rolled on a spool is at first wrapped in an envelope containing silver amalgam or in paper which has been coated with silver amalgam. The film is then placed in the original lightproof wrapping. After about 3 days the latent image has been sufficiently intensified so that a much more contrasty negative will be obtained. In the event that the film had been underexposed, a sufficiently contrasty picture will be produced.

Example 6.—A film is brought into contact with or wrapped in a copper foil which has been treated with mercury or mercury vapor to form an amalgam surface thereon. The hypersensitizing effect of the foil will be noticeable after a few days.

The same result may be obtained by employing a foil of zinc, tin, or silver, similarly treated with mercury or mercury vapor to produce an amalgam on the surface thereof.

Example 7.—A film is brought into contact with or is wrapped in a photographic paper which has been exposed to light, developed, fixed, washed, dried and treated with mercury or mercury vapor. After a few days the film will have been found to have been hypersensitized by the thus treated paper.

Example 8.—Photographic film is maintained in contact with zinc amalgam during the manufacture of the same, to wit during drying, cutting, spooling and storing. As a result of this treatment a much more sensitive film is obtained.

Example 9.—Bulk film is subjected to the action of silver amalgam in the original cans for a period of from 5 to 8 days. The film is thereby uniformly sensitized over the entire length of the roll.

It is not practical to have the photographic material remain too long in contact with the amalgam for the reason that prolonged treatment causes fog. In most cases it was possible to reach the maximum effect in 3 to 8 days. After that period of time, fog became noticeable so that it may be said that for most purposes the time stated represents the maximum duration of treatment.

I have also observed that protographic material which had been hypersensitized according to the present invention gradually but noticeably loses the additional sensitivity resulting from the influence of the amalgam after storing for a period of about 4 weeks. It has been determined, however, that this loss in sensitivity can be obviated if the "dry hypersensitized" material is stored at a temperature below 0° C. until it is required for use. Thus a dry hypersensitized film, which had been stored for about 7 weeks at room temperature, lost all the additional speed imparted thereto by treatment with amalgam. The same type of film, however, when stored for the same period of time at a temperature of minus 10° C. retained the additional speed obtained by treatment with amalgam. A further important factor of the present invention, therefore, includes the idea of maintaining the film at a relatively low temperature during storage in order to insure that the film will retain the additional sensitivity imparted thereto. It may be added in passing, however, that photographic material which has lost its hypersensitivity through storing may be again hypersensitized by resubmitting the material to the action of the amalgam.

Various changes and modifications may be made in the invention without departing from the scope thereof and without the sacrifice of any of the advantages derivable therefrom. Thus for example the invention contemplates the manufacture of paper by working the amalgam into the pulp of the paper and utilizing the paper to effect hypersensitizing by bringing the paper into contact with wrapped or unwrapped photographic material.

Throughout the claims the term "photographic emulsion" is to be construed as meaning either an unexposed emulsion or an exposed but undeveloped emulsion.

What is claimed is:

1. Process for dry hypersensitizing photographic silver halide emulsions comprising closely associating said emulsions with an amalgam and subjecting the emulsions to the action of said amalgam for sufficient time to substantially hypersensitive said emulsions.

2. Process for dry hypersensitizing photographic silver halide emulsions comprising closely associating said emulsions with an amalgam selected from the class consisting of the amalgams of silver, copper, tin and zinc and subjecting the emulsions to the action of said amalgam for sufficient time to substantially hypersensitive said emulsions.

3. Process for dry hypersensitizing photographic silver halide emulsions comprising closely associating said emulsion with an amalgam and subjecting the emulsions to the action of said amalgam for a period of from about 12 hours to 8 days.

4. Process for dry hypersensitizing photographic silver halide emulsions comprising closely associating said emulsions with an amalgam selected from the class consisting of silver, copper, tin and zinc and subjecting the emulsions to the

action of said amalgam for a period of from about 12 hours to 8 days.

5. Process for dry hypersensitizing and insuring the maintenance of the hypersensitivity of photographic silver halide emulsions comprising closely associating said emulsions with an amalgam and subjecting the emulsions to the action of said amalgam for sufficient time to substantially hypersensitize said emulsions and maintaining the emulsion at a temperature below 0° C. during storage.

6. Process for dry hypersensitizing the photographic silver halide emulsion of a roll film which comprises closely associating said emulsions with an amalgam and subjecting said film to the action of about one tenth to one half gram of said amalgam for a period of about 12 hours to 8 days.

FRITZ H. DERSCH.