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2,976,149

DIRECT POSITIVE PHOTOGRAPHIC EMULSION

**Irma De Maria and Vincent De Maria, Freeport, N.Y.,
assignors to Repro Design & Equipment Company,
Inc., Freeport, N.Y., a corporation of New York**

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This invention relates to a photographic emulsion based upon a silver halide which upon exposure to light and subsequent development directly produces positive copies of the original image.

In the art of photography, as it is practiced today, it is customary first to obtain a negative transparency of the original image and then utilize the transparency in the production of positive prints. In a negative, as the term is employed in photography, the light parts of the object appear as shadows and the shadows as highlights. In a positive, the highlights and shadows correspond directly to the original object. Production of a positive print from the negative transparency is based upon the simple fact that light passed through the transparency upon photographic paper will convert the shadows of the transparency into highlights and the highlights into shadows.

This procedure, although requiring two steps, has reached a far more refined state of development than the production of direct positives. Many efforts have been made to eliminate the necessity of producing a negative transparency, and directly obtain a positive copy of the original object. These methods have not met with success because the results obtained have not been comparable in quality with those available with the intermediate negative method.

Many of these efforts have been along the lines of the well-known phenomenon of reversal or solarization. However, positive images produced in this way have proved unsatisfactory for two reasons. Inordinately large exposure times are required for reversal, which, of course, greatly restricts the possibilities for use of such emulsions. Furthermore, upon development, the reversed image does not prove of acceptable density. Increasing the exposure beyond certain limits brings about re-reversal. Increased development time produces overall fog. This probably is due to the fact that the solarization reduces the developability of the grains but with continued action of the developer, the resistance of the grains to development is overcome, and metallic silver eventually is produced from all of the exposed grains.

Many efforts have been made to overcome the problems presented in utilizing solarization to produce direct positive images. Any substance which has the faculty of increasing the sensitivity of an emulsion, whether that be in the area of color or speed, is a sensitizer, and many such substances have been incorporated in the photographic emulsions to increase the sensitivity to light of the emulsion. These, however, usually increase sensitivity in the range of the rays of long wave length, but reduce it in the range of rays of short wave length. It also has been proposed to fog the emulsion prior to use by adding fogging agents, heating, exposing to light, or combinations of these methods, prior to coating the emulsion on the support. In U.S. Patent No. 2,005,837 fogged direct positive emulsions are prepared by incorporating into the emulsion a substance which causes fog, and then heating it. British Patent No. 443,245 describes the production of fogged emulsions by treatment with X-rays. German

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Patent No. 693,917 fogs emulsions by treatment with ultraviolet visible or infrared rays. Fogging has, however, the effect of reducing the sensitivity of the emulsion to light, as would be expected. U.S. Patent No. 2,323,187 seeks to overcome this effect by incorporating extraordinarily large amounts of sensitizers to the emulsion in addition to the fogging treatment. Even this expedient has not, however, been successful.

U.S. Patent No. 2,184,013 seeks to avoid fogging and the problems entailed thereby altogether by adding a non-acid optical sensitizing dye to the emulsion together with small amounts of photographic developers along with optical sensitizers for the purpose of increasing the maximum density obtainable. The purpose of the dye is to impart reversal characteristics on prolonged exposure. These emulsions are said to have better contrast, and not to reverse in the region of overexposure. Significantly, the patent nowhere indicates what exposure times are required.

U.S. Patent No. 2,401,051 seeks to solve the problem by a different approach. Emphasis here is placed upon the formation of the silver halide grains during precipitation and/or first digestion under conditions favoring their adsorption of halogen or other substance capable of destroying the developability of said grains. The adsorption is aided by having the grain-forming precipitation and first digestion take place in a solution containing a soluble halide and hydrogen ions sufficient to make the solution definitely acid, the pH ranging from 4.7 to 2.5.

The methods disclosed in the patents and literature for making direct positive photographic emulsions are very similar to those used for the production of negative emulsions. It is customary to prepare a gelatin solution and dissolve in it a suitable quantity of an ammonium or other soluble halide, keeping the mass warm in a water bath. The silver halide then is precipitated by addition of an aqueous solution of silver nitrate, with stirring, the ammonium halide and the silver nitrate reacting to precipitate the silver halide. The purpose of the gelatin is to suspend the silver halide which is thus precipitated, and while the concentration of gelatin may be varied, it is never cut to the point where it is unable to suspend the precipitated silver halide. The resulting emulsion then is subjected to a digestion, accomplished by heating the emulsion for an indefinite period, which may be as long as several hours. This acts to increase the sensitivity of the silver halide grains. Additional gelatin and sensitizers may then be added and the emulsion chilled, shredded and washed. Next, the emulsion is subjected to a second digestion, which is effected by melting it and then heat-treating it at an elevated temperature. At this time, chemical sensitizers present in the emulsion can act to form light-sensitive silver sulfide nuclei on or in the silver halide crystals. The emulsion is then coated or spread on a suitable layer or support.

It is surprising to note that no one has suggested that the method of preparing direct positive photographic emulsions might advantageously differ from the method of preparing negative photographic emulsions. Undoubtedly, the reason for this is that it has not been recognized that such a difference would lead to a difference in result. Rather, it has been supposed that attention should be paid to the method of control of the developability of the emulsion, so as to increase the tendency of the emulsion toward solarization, and prevent the formation of a negative image. Such emphasis, of course, naturally follows the intense interest in the theoretical aspects of solarization, a phenomenon which to this day is not fully understood.

In accordance with the instant invention, it has been determined that the method of formation of the direct positive photographic emulsion is no less important than

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the composition of the emulsion itself. It is essential to form the silver halide precipitate in the absence of gelatin. For some reason which is not understood, formation of the silver halide grains in the presence of the gelatin is disadvantageous. It also is desirable that the silver halide grains be formed in the presence of one or a mixture of two or more accelerating agents.

Thus, in the process of the invention, the silver halide precipitate is formed by reacting a water-soluble silver salt and a metal halide in the presence of one or more accelerating agents. Thereafter, the precipitate is emulsified in a gelatin solution, and after digestion can be coated on a suitable support.

The direct positive photographic emulsion of the invention as thus prepared contains as the essential ingredients grains of a silver halide dispersed in gelatin together with the accelerators.

As the accelerator there can be used any accelerator employed in negative photographic emulsions. The preferred accelerators are thiourea, tannin and cupric oxide. The latter in the course of preparing the emulsion is probably converted into the corresponding cupric salt of the halide present in the emulsion. The accelerator must be soluble in water, or, if it is insoluble, must be solubilized in water by the addition of a suitable acid or alkali. Cupric oxide, for example, can be solubilized in an aqueous dilute nitric acid solution containing a sufficient amount of nitric acid, or in dilute ammonium hydroxide solution containing sufficient ammonia to form the soluble copper ammonia complex $\text{Cu}[\text{NH}_3]_4^{++}$.

The amount of accelerator is not critical. Preferably the proportion of accelerator to silver halide is that given in the example.

The concentration of silver halide in the gelatin emulsion is not critical. The amount used will, of course, determine the sensitivity, and the grain size will determine the speed of the emulsion.

The silver halide is formed in the presence of the accelerator by double decomposition, that is, by reaction of a water-soluble metal halide and a water-soluble silver salt, such as any alkali metal or ammonium halide, preferably a potassium halide, and silver nitrate. It is desirable to employ an excess of the soluble halide in this reaction, the excess being approximately 40 to 50% above that stoichiometrically required to react with the amount of silver salt employed. When these salts are interreacted, a precipitate of silver halide will form, and this will quickly precipitate because the reaction is carried out in the absence of gelatin. It is desirable to have present in the solution a sufficient amount of ammonium hydroxide to precipitate the silver as the silver ammonia complex $\text{Ag}[\text{NH}_3]_2\text{OH}$, and then just dissolve it. This ensures rapid precipitation of the silver halide. Precipitation of the silver halide enables its separation from the other salts which are still soluble at this stage, and makes it possible to blend the precipitated silver halide in a relatively pure condition with the gelatin solution.

It is also desirable to have sufficient ammonium hydroxide completely to dissolve the silver halide in the gelatin solution. The ammonium hydroxide maintains the silver halide in soluble form during the first digestion. The silver halide then is precipitated again during the second digestion by neutralizing the ammonium hydroxide with a halogen acid, the halogen being the same as the halogen of the silver halide, and in this way a final emulsion obtained containing precipitated grains of silver halide in the desired concentration and of the desired size.

In order to prepare the emulsion, the accelerators are dissolved in distilled water. A separate solution is formed of the soluble silver salt in distilled water, and the solution of the accelerators then is added to it.

Next, there is prepared an aqueous solution of an alkali metal halide in aqueous ammonium hydroxide solution. To this solution is added the aqueous silver salt solution

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containing the accelerators. The solution containing the precipitated silver halide is allowed to settle, and the supernatant liquid decanted and discarded. This procedure obviates the necessity for washing the emulsion since the decanted liquid contains the materials ordinarily removed by the washing.

The precipitated silver halide thus obtained then is added to an aqueous solution of gelatin and ammonium hydroxide which has been brought to a temperature of 170° F. The silver halide dissolves, and this solution is digested for several minutes over a hot water bath, until solution is complete. An acid halide is added to bring the pH to above 7, to reprecipitate the silver halide, and the solution then is digested at 120° F. until precipitation is complete, usually within one-half hour.

The following example is illustrative, and in the opinion of the inventors represents the best embodiment of their invention.

Example

There was prepared a solution containing 2 mg. thiourea and 2 mg. tannin in 25 cc. of distilled water. Separately, there was prepared a solution of 90 g. silver nitrate in 630 cc. of distilled water. To the last-mentioned solution there was added a solution of 900 mg. cupric oxide in 2 cc. of water and 2.5 cc. of concentrated nitric acid.

To the completed silver nitrate solution there was then added 2.5 cc. of the thiourea-tannin solution, diluted with 36 cc. of distilled water.

To a solution of 90 g. potassium bromide in 120 cc. of ammonium hydroxide and 300 cc. of distilled water, there was then added the completed silver nitrate-thiourea-tannin solution.

A precipitate of silver bromide formed. When precipitation was complete, the supernatant liquid was decanted.

A solution was prepared of 81 g. photographic gelatin in 165 cc. of ammonium hydroxide and in 900 cc. of distilled water. The gelatin was soaked in the water, dissolved by heating over a hot water bath, and the ammonium hydroxide added.

To this solution warmed to 170° F., was added the silver bromide precipitate. The resulting solution was digested for 10 minutes over a hot water bath, until all of the halide had dissolved. There was then added 54 cc. of hydrobromic acid, whereupon the silver halide reprecipitated, and the mixture was digested for another ½ hour at 120° F.

The resulting emulsion was coated on paper of the type used in preparing ordinary photographic paper. The resulting coated direct positive photographic paper was very fast, and a good positive image could be obtained by contact printing with only 2 seconds' exposure. The print was developed using ordinary photographic developers recommended for bromide papers.

The direct positive photographic emulsions in accordance with the invention can be coated upon any of the supports currently in use in photography. They can, for example, be coated on transparent or opaque supports, for instance, paper, glass, photographic film, metal and plastic surfaces; for instance, polyvinyl chloride film, polyvinylidene chloride film, transparent film made from polymers of terephthalic acid and ethylene glycol, cellophane, and the like.

We claim:

1. The process for producing, in the absence of gelatin, silver halide grains in a relatively pure condition for mixing with gelatin to form a direct photographic emulsion, which comprises mixing together in an aqueous solution a soluble silver compound capable of reacting with halide to form silver halide and ammonium hydroxide in an amount sufficient to solubilize the silver present as the silver ammonia complex $\text{Ag}(\text{NH}_3)_2\text{OH}$, a halide compound capable of reacting with silver to pro-

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duce silver halide, the said halide compound being in an amount at least 40% greater than the amount stoichiometrically required to precipitate silver halide, and an accelerator selected from the group consisting of thiourea, tannin and cupric oxide promoting formation of silver halide grains, said solution consisting of the said ingredients and waters, thereby obtaining a precipitate of silver halide grains, separating the grains from the residual solution, and then mixing the grains with an aqueous gelatin solution.

2. A process in accordance with claim 1 in which the halide is bromide.

3. A process for the preparation of direct positive photographic emulsions which comprises mixing together in aqueous solution a soluble silver compound capable of reacting with a halide compound to produce silver halide, and ammonium hydroxide in an amount to solubilize the silver present as the silver ammonia complex $\text{Ag}(\text{NH}_3)_2\text{OH}$, a halide compound capable of reacting with silver to produce silver halide, the said halide compound being in an amount at least 40% greater than the amount stoichiometrically required to precipitate silver halide, and an accelerator selected from the group consisting of thiourea, tannin and cupric oxide, promoting formation of silver halide grains, said solution consisting of the said ingredients and water, thereby obtaining a precipitate of silver halide grains, allowing the precipitated silver halide to settle, removing the supernatant liquid, dissolving the precipitated silver halide in an aqueous solution of gelatin and ammonium hydroxide, digesting the solution at an elevated temperature, if necessary, to complete solution of silver halide, adding a halogen acid liberating the same halogen ion as the silver

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halide in aqueous solution in an amount sufficient to bring the pH to below 7 and reprecipitate the silver halide, and digesting the resulting mixture until precipitation of silver halide is complete.

4. A direct positive photographic emulsion comprising an accelerator and grains of a precipitated silver halide dispersed in gelatin, said silver halide having been prepared in accordance with the process of claim 1.

5. A direct positive photographic emulsion comprising an accelerator and grains of precipitated silver bromide dispersed in gelatin, said silver bromide having been prepared in accordance with the process of claim 2.

6. A direct positive photographic emulsion comprising an accelerator and grains of a precipitated silver halide dispersed in gelatin, said emulsion having been prepared in accordance with the process of claim 3.

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