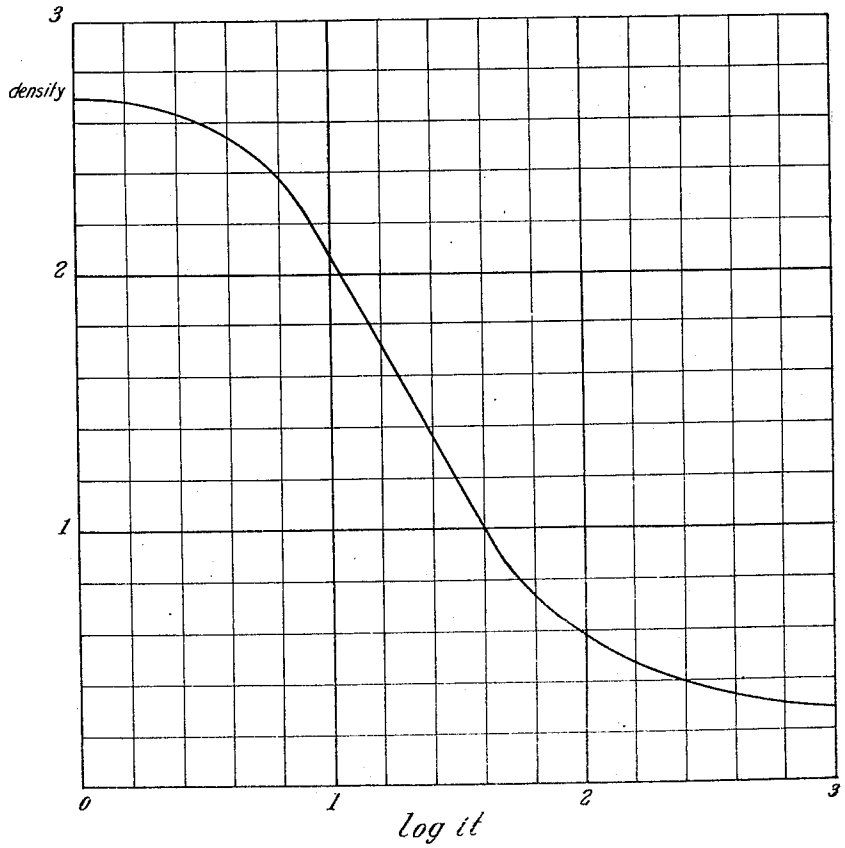
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MANUFACTURE OF PHOTOGRAPHIC EMULSIONS

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MANUFACTURE OF PHOTOGRAPHIC EMULSIONS

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My present invention relates to silver halide gelatin emulsion layers.

One of its objects is to provide a process of manufacturing such emulsions which after developing directly give positives. Another object are the emulsions directly yielding positives which show no fog at the places of highest illumination. Reference is made to the accompanying drawing which illustrates the gradation curve of an emulsion as obtainable by my invention.

As is known the blackening of a light-sensitive photographic silver halide emulsion layer reaches, with an increasing illumination, a maximum value and then diminishes again. In that part of the gradation curve which lies beyond the apex and which is named the solarization region, the density, in spite of further increasing the illumination is progressively diminished. It has already been proposed preliminarily to expose, for the preparation of direct positives, a silver halide emulsion layer, previous to the proper exposure, until the solarization limit is obtained, so that by the subsequent exposure the nuclei capable of development uniformly produced in the whole layer are made insensitive to development in picture-forming gradation. However, such an emulsion layer which has been subjected to preliminary exposure, is of no practical value, because it has an insufficient gradation, i. e. a too flat gradation, because of the application of the preliminary exposure on commercial scale is associated with great difficulties.

This invention is based on the observation that by causing a strong fog on a silver halide emulsion and bringing the emulsion thus prepared to strong solarization (by heating the fogged emulsion to a high temperature for a short time or to a lower temperature for a longer time) yields an emulsion which is suitable for the direct production of positives by exposure and development. This result is attained by the addition to the emulsion of substances, which cause fog whereby a solarization curve is obtainable the course of which is similar to that of the normal gradation curve. These substances have the property of forming nuclei capable of development in the emulsion in an extent which corresponds with the formation of such nuclei by exposure to light of the emulsion until the apex of the gradation curve is reached, that is when adding said substances in a sufficient quantity that they cause a fog which corresponds with the maximum blackening of an usual emulsion that amounts, for instance, to the value 3 measured by the Martens sensitometer. Suitable substances which cause fog are, for instance, silver nitrate, the known photographic ripening substances, for instance, products of decomposition of vegetable or animal proteins prepared by alkaline or alkaline fermentative hydrolysis and a simultaneous partial oxidation (cf. U. S. Patent No. 1,719,711) or proteins prepared by acid hydrolysis and simultaneous partial oxidation (cf. U. S. Patent No. 1,815,983) or thiazole compounds (cf. U. S. Patent No. 1,725,934), or mixtures of these compounds, furthermore reducing compounds such as developing substances, for instance, hydroquinone, paraphenylendiamine, amidol which are preferably used in admixture with ripening substances. The substances may be added to the emulsion in the emulsifying process or in an after-treatment which is preferably carried out after washing the emulsion. It has proved advantageous to heat the emulsion. If the emulsion is heated to a high temperature heating can be shortened and if the emulsion is heated to a lower temperature the heating operation must be carried on for a prolonged time, for instance, when heating the emulsion to 100° C. the duration will be about half an hour, however, when heating the emulsion only to 45° C. heating must be continued for about 20 to 24 hours. When incorporating in the emulsion an excess of silver nitrate there is preferably used an excess of ammonia; if there is no excess of ammonia present the emulsions must be heated for a longer time and eventually to a higher temperature. When using the above enumerated ripening substances the excess of ammonia may be omitted without the necessity of heating the emulsion longer or to a higher temperature for this reason. The substances are added while dissolved in a suitable solvent; in most cases water will do. If a finished emulsion, that is an emulsion that has already been washed, is to be subjected to the treatment according to this invention a solution of one or more of the said substances is added to the emulsion ready for being cast and finely distributed therein. The emulsion is then heated as already described. It may be pointed out that not all finished emulsions give the same good results but all emulsions which after a preliminary exposure show a suitable solarization curve will and are made with a weakly ripening gelatin show at least the same good solarization curve when treated according to my process.

The following examples serve to illustrate my invention.

Example 1.—In this example there is instanced

the manufacture of an emulsion showing a good solarization curve. The following three solutions are prepared for this purpose:

Solution 1

10 grams of gelatin
46 cc. of a 10 per cent solution of ammonium bromide
3 cc. of a 10 per cent solution of potassium iodide
50 cc. of water

Solution 2

100 cc. of a 10 per cent solution of silver nitrate to which so much of a 25 per cent solution of ammonia has been added that the precipitating silver hydroxide is again dissolved

Solution 3

10 grams of gelatin
34 cc. of a 10 per cent solution of ammonium bromide
1 cc. of a 10 per cent solution of potassium iodide
15 cc. of water

These solutions are mixed by first heating Solutions 1 and 2 to about 80° C. and then adding Solution 1 to Solution 2. This mixture is kept at about 90° C. for about ½ hour. Hereafter Solution 3 is heated to about 80° C. and added to the mixture of Solutions 1 and 2. Heating is still continued for about 6 minutes, whereupon the whole is cooled. The hardened emulsion is then washed and worked up as usual. In casting 6 cc. of a 10 per cent solution of ammonium bromide may be added to the emulsion. The operation is carried out in an open vessel so that the ammonia can partially evaporate during heating.

Example 2.—An emulsion which shows a good solarization curve is prepared, for instance, by means of a weakly ripening gelatin, as follows: To 100 cc. of a solution containing 10 per cent of gelatin there were added 8 grams of ammonium bromide and 0.3 gram of potassium iodide. To this solution there was added at a temperature of 43° C. 100 cc. of an ammoniacal solution containing 10 per cent of silver nitrate heated rather quickly and the emulsion was ripened at 45° C. After half an hour 10 grams of dry gelatin reduced to small pieces were added. The emulsion is washed with water and then molten. To the molten emulsion there is added one of the known ripening substances, for instance, to 1 kilo of emulsion 10 milligrams of gelatin treated as follows: 2.6 grams of gelatin are boiled with 0.2 gram of colloidal sulfur or heated in an autoclave with 10 grams of carbon disulfide in slightly acid solution during 1 hour; the uncombined carbon disulfide is removed by distillation, and 5 cc. of a 10 per cent solution of potassium iodide. Hereafter the emulsion is heated to 90° C. for about ½ hour. The addition of potassium iodide serves for increasing the sensitiveness. After this treatment the emulsion is ready for being worked up.

Example 3.—The mode of operation is the same as in Example 1 with the following exceptions: Solution 1 is made with only $\frac{1}{5}$ to $\frac{1}{3}$ of the weight of gelatin indicated in Example 1, and 0.25 milligram of ripening substance, for instance, thiosinamine is added in its stead. The amount of gelatin which has been omitted in Solution 1, is then added to Solution 3, so that the total amount of gelatin is the same as in Example 1.

Example 4.—The mode of operation is according to Example 1 with the difference that the silver nitrate is dissolved in water and 50 per cent of the ammonia which was necessary for dissolving the silver nitrate is added to Solutions 1 and 3 in the ratio 3:1.

The action of the substance which causes fog must of course be compensated after the desired effect is obtained. This is generally effected by removing the fogging substance in the washing operation or for instance in the case of Example 1 the silver nitrate is converted after having effected its fogging action into silver halide.

The light sensitive substance incorporated in the emulsions made according to my invention should comprise at least 50 per cent of silver bromide. The sensitiveness of the emulsions and the density of the pictures made therewith are improved when at least a small amount of silver iodide is incorporated in the emulsion, for instance, 5 per cent or less. Emulsions suitable for the process are also such as are obtainable by peptization of a silver bromide deposit in gelatin. Very good results are obtainable when adding to the Solutions 1 and 3 in Example 1 a small quantity of ammonia. As already mentioned in Example 1 the operation should be carried out in an open vessel, however, I may likewise neutralize a certain amount of the ammonia by adding an acid. This quantity can be easily determined by experiment. As a rule at least 30 per cent of the added ammonia should be neutralized, but at least 10 per cent of ammonia should remain in the mixture until washing of the emulsion. Furthermore, it has proved advantageous to add only part of the whole quantity of gelatin to be used for the production of the emulsion in the emulsifying operation proper and to add the rest in form of dry gelatin while cooling the emulsion before washing. To the emulsions there may be applied, if desired, dyestuffs as usual in photography, for instance, bleaching-out dyes, such as phenosafranine and fuchsine or sensitizers or filter dyes.

In the annexed drawing there is shown the gradation curve of an emulsion produced according to my invention. The abscissæ are marked in the usual measure of log. *it*, while the ordinates denote blackenings of the emulsion when developed for 5 minutes with standard developer according to the proposition of Luther, measured in the usual density units. The emulsion made according to the process described bleach out to a clearness of 0.8 density unit and below and even to 0.4 and below.

The invention is not limited to the above examples or to the specific details given therein. Many changes of details will occur to those skilled in the art without departing from the scope of the invention.

What I claim is:

1. The process of manufacturing photographic emulsion layers directly yielding positive pictures which comprises producing a strongly fogged silver halide emulsion by the addition of a substance which causes fog and bringing the fogged emulsion to strong solarization.

2. The process of manufacturing photographic emulsion layers directly yielding positive pictures which comprises incorporating in the silver halide gelatin emulsion a compound which causes fog and heating the emulsion to a temperature within the range of about 45° to 100° C. until the blackening corresponds with that of the apex of the gradation curve.

3. The process of manufacturing photographic emulsion layers directly yielding positive pictures which comprises incorporating in the silver halide gelatin emulsion a compound selected from the group consisting of silver nitrate, ripening substances, a reducing agent and mixtures thereof and heating the emulsion to a temperature within the range of about 45° to 100° C. until the blackening corresponds with that of the apex of the gradation curve.

4. The process of manufacturing photographic emulsion layers directly yielding positive pictures which comprises preparing a first solution containing gelatin, ammonium bromide, potassium iodide and water, a second solution containing silver nitrate, ammonia and water, and a third solution comprising gelatin, ammonium bromide, potassium iodide and water, mixing the first and the second solution after heating the same to about 80° C. and keeping the mixture for about ½ hour at about 90° C., and then adding the third solution.

5. The process of manufacturing photographic emulsion layers directly yielding positive pictures which comprises preparing a first solution containing gelatin, ammonium bromide, potassium iodide, ammonia and water, a second solution containing silver nitrate and water, a third solution containing gelatin, ammonium bromide, potassium iodide, ammonia and water, mixing the first and the second solution after heating the same to about 80° C. and keeping the mixture for about ½ hour at about 90° C., and then adding the third solution.

6. The process of manufacturing photographic emulsion layers directly yielding positive pictures which comprises preparing a first solution containing gelatin, a ripening substance, ammonium bromide, potassium iodide, ammonia and water, a second solution containing silver nitrate and water, a third solution containing gelatin, ammonium bromide, potassium iodide and water, mixing the first and the second solution after heating the same to about 80° C. and keeping the mixture for about ½ hour at about 90° C., and then adding the third solution.

7. The process of manufacturing photographic emulsion layers directly yielding positive pictures which comprises melting a silver halide emulsion, adding a ripening substance to the molten emulsion and heating the emulsion to about 90° C. until the blackening corresponds with that of the apex of the gradation curve.

8. The process of manufacturing photographic emulsion layers directly yielding positive pictures which comprises melting a silver halide emulsion, adding 10 mgrs. of the ripening substance obtained by boiling 2.6 grams of gelatin with 0.2 gram of colloidal sulfur in slightly acid solution, and 5 cc. of a 10 per cent solution of potassium iodide to 1 kilo of the molten emulsion and heating the emulsion to about 90° C. for about ½ hour.

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