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PHOTOGRAPHIC PRINTING MATERIAL

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This invention relates to photographic printing material and more particularly to photographic material giving various degrees of contrast.

To prepare a photographic silver halide printing material which gives rise to various degrees of contrast under the same conditions of development, it has been proposed to coat in layers, or to mix together, two different silver halide emulsions having different contrasts (gamma). Thus, an emulsion which works hard and is sensitive to blue (such as a silver chloride emulsion) can be mixed with an emulsion which works soft and is sensitive to green (such as a spectrally sensitized silver bromide emulsion). If such a composite emulsion is exposed to light passing through a blue-green filter, the emulsion works normally and is suitable for negatives of normal gradation (contrast). If, however, it is desired to print from a negative with strong contrasts, the light which acts upon the emulsion which works hard is cut off by means of a filter permeable only to green, and a normal picture is obtained by means of the emulsion which works soft. If, on the other hand, it is desired to print from a negative with but little contrast, the light which acts upon the emulsion which works soft is cut off by means of a filter permeable only to blue, and a normal picture is obtained by means of the emulsion which works hard.

A variation of the above process involves the sensitization of the contrasty chloride emulsion instead of the softer bromide emulsion, to the green portion of the spectrum.

We have now found that advantageous results can be obtained by mixing together silver chloride emulsions of different contrast, the emulsions having different contrasts, the emulsions being sensitive to different spectral regions, and the emulsion of the lower contrast containing a small amount of silver bromide, i. e. up to about 5% by weight of the silver halide in the emulsion of lower contrast. The image shades given by the two silver halides of substantially the same chemical composition can be more nearly alike than when different silver halides are employed. By using substantially the same silver halides rather than different ones, the time of development is more constant over the whole range of contrasts when the same developing solution is used; indeed the nature of the developing solution is of less importance, so that satisfactory results can be obtained with a variety of developing solutions. If any addition (e. g. potassium bromide) is made to the developing solution, the effect thereof will be more nearly the same over the whole range than when the emulsions involved are different. Moreover, by incorporating a small amount of silver bromide in the silver chloride emulsion of lower contrast, the diffusion of sensitizing dyes from the grains of the one emulsion to the grains of the other is markedly decreased.

It is, accordingly, an object of our invention to provide a photographic printing material which gives various degrees of contrast. A further object is to provide a process for preparing such materials. Other objects will become apparent hereinafter.

In accordance with one embodiment of our invention, two silver chloride emulsions of different contrasts and different violet sensitivities are employed, and the harder of these is color sensitized, say to the blue or blue-green, with a sensitizing dye. The violet sensitivities of the two emulsions should be widely separated, so that, through a violet filter, the soft component is substantially fully exposed before the hard emulsion registers. The emulsion of lower contrast (the soft emulsion) is prepared to contain a small amount of silver bromide, the silver bromide content being not more than about 5% by weight of the total silver halide in the emulsion of lower contrast. The following example will serve to illustrate an emulsion prepared in accordance with this embodiment of our invention.

Example 1

A hard washed gelatino-silver-chloride developing-out emulsion was prepared in the usual manner, except that after emulsification, 5-(3-ethyl-2(3)-benzoxazolylidene-ethylidene)-3-(n-heptyl)-1-phenyl-2-thiohydantoin was added to the emulsion in a concentration of 0.005 g. per 100 g. of silver nitrate used in preparing the emulsion. The emulsion was held at about 45° C. for about 30 minutes after addition of the dye. A soft washed gelatino-silver-chloride developing-out emulsion was prepared containing about 3% of silver bromide and about 1% by weight of silver iodide based on the total weight of silver halide in the emulsion and having a speed to violet light considerably greater (2 to 10 times) than that of the hard emulsion. The two emulsions were then mixed in equal proportions at C. The mixed emulsion was then coated to desired weight upon a suitable support of paper, glass, cellulose derivative or resin and dried in the usual manner. Such a mixed emulsion when exposed with violet light works soft for ordinary

exposures and when exposed through a filter which cuts out violet light works hard.

In accordance with a further embodiment of our invention, two silver chloride emulsions of different contrasts and different violet sensitivities are employed, and the harder of these is sensitized to the green with a sensitizing dye, while the softer emulsion is sensitized to the blue. While the violet sensitivities of the two emulsions should not be too near in practicing this embodiment of our invention, it is less important to have a wide separation in sensitivities than it is in the foregoing embodiment. The emulsion of lower contrast (the soft emulsion) is prepared to contain a small amount of silver bromide, the silver bromide content being not more than about 5% by weight of the total silver halide in the emulsion of lower contrast. The following example will serve to illustrate an emulsion prepared in accordance with this embodiment of our invention.

Example 2

A hard washed gelatino-silver-chloride developing-out emulsion was prepared in the usual manner, except that after emulsification, 5-(3-ethyl-2(3)-benzoxazolylidene-ethylidene)-3-(-n-heptyl)-1-phenyl-2-thiohydantoin was added to the emulsion in a concentration of 0.005 g. per 100 g. of silver nitrate used in preparing the emulsion. The emulsion was held at about 45° C. for about 30 minutes after addition of the dye. A soft washed gelatino-silver-chloride developing-out emulsion was prepared containing about 3% of silver bromide and about 1% by weight of silver iodide based on the total weight of silver halide in the emulsion and having a speed to violet light greater (2 to 10 times) than that of the hard emulsion. After emulsification, 3-(n-heptyl) - 5-(1-methyl-2-β-naphthoxazolylidene)-rhodanine was added twenty minutes before ripening was completed, in a concentration of 0.01 g. per 100 g. of silver nitrate used in preparing the emulsion. The two emulsions were then mixed in equal proportions at 30° C. The mixed emulsion was then coated to desired weight upon a suitable support of paper, glass, cellulose derivative or resin and dried in the usual manner. Such a mixed emulsion when exposed through a yellow filter (Wratten No. 5) works hard and when exposed through a blue filter (Wratten No. 47A) works soft.

Practiced in accordance with any of the embodiments, it is advantageous to employ a quantity of silver bromide in the silver chloride emulsion of lower contrast equal to from about 1% to about 5% of the weight of the total silver halide in the emulsion of lower contrast, although quantities less than 1% give beneficial effects.

The ratio of contrasts between the two emulsions which are mixed can be any desired ratio. However, the gradation of the hard emulsion is advantageously at least 2.5 times greater than that of the soft emulsion.

In practicing our invention, the sensitizing dyes employed should be capable of withstanding a digestion at about 45° C. for about one-half hour, since such a digestion of the emulsion containing the sensitizing dye appears to increase the firmness with which the dyes are adsorbed to the silver chloride. Moreover, most chloride emulsions are usually ripened (digested) in the presence of an acid, such as citric acid or hydrochloric acid, so that the dye should be capable of withstanding the aforesaid digestion in an acid medium.

What we claim as our invention and desire to secure by Letters Patent of the United States is:

1. A photographic printing material comprising a mixture of two silver chloride emulsions at least one of the emulsions containing a sensitizing dye so that the emulsions have different spectral sensitivities, one of the emulsions having a contrast at least 2.5 times greater than that of the other emulsion, the emulsion of lower contrast having a speed to violet light at least twice as great as the speed to violet light of the emulsion of higher contrast, the emulsion of lower contrast containing silver bromide in a concentration equal to not more than about 5 percent by weight of the silver halide in the emulsion of lower contrast.

2. A photographic printing material comprising a mixture of two gelatino-silver-chloride emulsions at least one of the emulsions containing a sensitizing dye so that the emulsions have different spectral sensitivities, one of the emulsions having a contrast at least 2.5 times greater than that of the other emulsion, the emulsion of lower contrast having a speed to violet light at least twice as great as the speed to violet light of the emulsion of higher contrast, the emulsion of lower contrast containing silver bromide in a concentration equal to not more than about 5 percent by weight of the silver halide in the emulsion of lower contrast.

3. A photographic printing material comprising a mixture of two gelatino-silver-chloride developing-out emulsions at least one of the emulsions containing a sensitizing dye so that the emulsions have different spectral sensitivities, one of the emulsions having a contrast at least 2.5 times greater than that of other emulsion, the emulsion of lower contrast having a speed to violet light at least twice as great as the speed to violet light of the emulsion of higher contrast, the emulsion of lower contrast containing silver bromide in a concentration equal to not more than about 5 percent by weight of the silver halide in the emulsion of lower contrast.

4. A photographic printing material comprising a mixture of two silver chloride emulsions at least one of the emulsions containing a sensitizing dye so that the emulsions have different spectral sensitivities, one of the emulsions having a contrast at least 2.5 times greater than that of the other emulsion, the emulsion of lower contrast having a speed to violet light from two to ten times greater than the speed to violet light of the emulsion of higher contrast, the emulsion of lower contrast containing silver bromide in a concentration equal to from about 1 percent to about 5 percent of the weight of the silver halide in the emulsion of lower contrast.

5. A photographic printing material comprising a mixture of two gelatino-silver-chloride emulsions at least one of the emulsions containing a sensitizing dye so that the emulsions have different spectral sensitivities, one of the emulsions having a contrast at least 2.5 times greater than that of the other emulsion, the emulsion of lower contrast having a speed to violet light from two to ten times greater than the speed to violet light of the emulsion of higher contract, the emulsions of lower contrast containing silver bromide in a concentration equal to from about 1 percent to about 5 percent of the weight of the silver halide in the emulsion of lower contrast.

6. A photographic printing material comprising a mixture of two gelatino-silver-chloride developing-out emulsions at least one of the emul-

sions containing a sensitizing dye so that the emulsions have different spectral sensitivities, one of the emulsions having a contract at least 2.5 times greater than that of the other emulsion, the emulsions of lower contrast having a speed to violet light from two to ten times greater than the speed to violet light of the emulsion of higher contract, the emulsion of lower contract containing silver bromide in a concentration equal to from about 1 percent to about 5 percent of the weight of the silver halide in the emulsion of lower contract.

7. A photographic printing material comprising a mixture of two gelatino-silver-chloride developing-out emulsions, one of the emulsions having a contrast at least 2.5 times greater than that of the other emulsion, the emulsion of lower contrast having a speed to violet light from two to ten times greater than the speed to violet light of the emulsion of higher contrast, the emulsion of lower contrast containing 5-(3-ethyl-2-(3)-benzoxazolylidene-ethylidene)-3-(n-heptyl)-1-phenyl-2-thiohydantoin and containing silver bromide in a concentration equal to from about 1 to about 5 percent by weight of the silver halide in the emulsion of lower contrast.

8. A photographic printing material comprising a mixture of two gelatino-silver-chloride developing-out emulsions one of the emulsions having a contrast at least 2.5 times greater than that of the other emulsions, the emulsion of lower contrast having a speed of violet light from two to ten times as great as the speed to violet light of the emulsion of higher contrast, the emulsion of higher contrast containing 5-(3-ethyl-2-(3)-benzoxazolylidene-ethylidene)-3-(n-heptyl)-1-phenyl-2-thiohydantoin, the emulsion of lower contrast containing 3-(n-heptyl)-5-(1-methyl-2-β-naphthoxazolylidene)-rhodanine and containing silver bromide in a concentration equal to from about 1 to about 5 percent by weight of the silver halide in the emulsion of lower contrast.

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