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METHOD OF MAKING A BLEND OF FOGGED, DIRECT POSITIVE SILVER HALIDE EMULSIONS OF DIFFERENT GRAIN SIZES

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ABSTRACT OF THE DISCLOSURE

A method of making a photographic element having at least one layer containing a blended grain silver halide emulsion, wherein the average grain size of at least two component emulsions of the blend differs by at least 50%, which comprises: preparing the respective component silver halide emulsions, blending the silver halide component emulsions, coating said emulsion blend on a support and reducing the liquid content of the coated blend; the improvement which comprises deferring the blending of the component emulsions of different grain size until just prior to coating and thereupon admixing the component blends and promptly thereafter coating the freshly formed admixture on the support whereby the support is coated with the minimum possible time delay between the time of admixing and the time of coating.

This invention relates to new processes for coating silver salt photographic emulsions. In one embodiment, this invention relates to new methods for coating admixtures of silver salt emulsions wherein said admixture comprises aliquot amounts of monodispersed grains of different grain sizes. In another embodiment, this invention relates to novel means for obtaining layers of silver halide emulsions having a fine grain emulsion in admixture with a coarse grain emulsion.

It is known in the art that extended latitude in photographic emulsions can be obtained by mixing silver halides of various grain sizes, such as disclosed in British Pat. 732,691. It is also known in the art that Ostwald ripening occurs when a fine grain silver halide emulsion is mixed with a coarse grain silver halide emulsion, the larger grains growing at the expense of the smaller grains. Therefore, it has been impractical in many instances to use mixed grain size emulsions to obtain extended exposure latitude, especially where long holding times were necessary in the coating operation before a given batch of emulsion is coated. The exposure characteristics of the last coated film are substantially altered from the characteristics at the start of the coating. This is especially a problem when fine grain emulsions having an average grain size of less than about 2 microns in diameter are utilized in the admixture wherein at least one component of the blend has an average grain size of at least 0.3 micron.

We have now found that silver salt emulsions comprising an admixture of silver salt grains of different average diameter sizes can be coated with substantially

uniform exposure characteristics throughout the coating run if the individual emulsions to be blended are held in separate vessels until just prior to coating, e.g., no more than about 2 minutes prior to coating. The respective emulsions are vigorously mixed prior to coating with good homogeneity in various mechanical mixing devices. A typical apparatus suitable for this purpose is disclosed in U.S. Pat. 2,912,343 issued Nov. 10, 1959.

In a preferred embodiment of this invention, direct-positive emulsions comprising various sizes of fogged silver halide grains are coated by the above process.

In another preferred embodiment, at least two monodispersed silver halide emulsions, wherein the average grain size of the second emulsion is at least 50% greater than the first, are effectively coated by this process.

In another preferred embodiment of this invention, the respective emulsions of different grain size are admixed within one minute prior to coating.

According to the present invention, the various silver halide portions to be combined to achieve the improved photographic properties are intimately admixed in the required proportion at or near the cotaing device and the mixture is coated within the minimum possible time delay between the time of mixing and the time when the emulsion is coated. The emulsion is then set and dried with the minimum of delay. The emulsion is generally mixed within 2 minutes of coating and preferably within 1 minute of the coating of the layer. The emulsion is then set and dried to no more than 15% moisture or liquid carrier within about 30 minutes. A typical apparatus for mixing the emulsions is disclosed in U.S. Pat. 2,912,343. Typical coating apparatus are disclosed in U.S. Pat. 2,761,791.

The process of this invention generally provides improved photographic emulsions with admixtures of any silver salt composition. Good results are obtained wherein at least one of the emulsions to be blended has an average grain size at least 50% greater and preferably 100% greater than one other component emulsion of the admixture. In a preferred embodiment, the largest improvements in photographic properties are obtained wherein a first emulsion having an average grain size of at least 0.3 micron is blended with another emulsion having an average grain size which differs by at least 50% in average size from said first emulsion.

Grain sizes can be measured by methods commonly used in the art for this purpose. A typical procedure is set forth by Loveland, "Methods of Particle-Size Analysis," ASTM Symposium on Light Microscopy, 1953, pages 94–122, or in chapter 2 of "The Theory of the Photographic Process," Mees and Jones, Third Ed. (1966), published by Macmillan Co. The grain size can be measured using the projected areas of the grains or approximate diameter. When the grains are substantially uniform in shape, the size distribution can be expressed quite accurately as either diameter or projected area.

The process of this invention is generally effective with any type of silver halide composition. However, especially good results have been observed when coating direct-positive silver halide emulsions. Typical emulsions

of this type are disclosed in Berriman, U.S. Pat. 3,367,778 issued Feb. 6, 1968, Illingsworth, U.S. Pat. 3,501,307 issued Mar. 17, 1970, Illingsworth, U.S. Pat. 3,501,306 issued Mar. 17, 1970, and Illingsworth and Spencer, Belgian Pat. 695,364 issued Sept. 11, 1967 corresponding to U.S. Pat. 3,501,310 issued Mar. 17, 1970.

In a highly preferred embodiment, monodispersed silver halide emulsions are coated by this process. Typical direct-positive silver halide emulsions of this type are disclosed in Illingsworth, U.S. Pat. 3,501,305 issued Mar. 17, 1970. Generally, in such emulsions, no more than about 5%, by weight, of the silver halide grains smaller than the mean grain size, and/or no more than about 5%, by number, of the silver halide grains larger than the mean grain size, vary in diameter from the mean grain diameter by more than about 40%. Preferred direct-positive photographic emulsions of this invention comprise fogged silver halide grains, at least 95%, by weight, of said grains having a diameter or projected area which is within 40%, preferably within about 30%, of the mean grain diameter or mean projected area, respectively. Average grain size can be determined using conventional methods, e.g., as shown in an article by Trivelli and Smith entitled "Empirical Relation between Sensitometric and Size-Frequency Characteristics in Photographic Emulsion Series," in The Photographic Journal, Vol. LXXIX, 1939, pages 330–338. The aforementioned uniform size distribution of silver halide grains is a characteristic of the grains in "mono-dispersed" photographic silver halide emulsions. Silver halide grains having a narrow size distribution can be obtained by controlling the conditions at which the silver halide grains are prepared using a double run procedure. In such a procedure, the silver halide grains are prepared by simultaneously running an aqueous solution of a water-soluble silver salt, for example, silver nitrate, and a water-soluble halide, for example, an alkali metal halide such as potassium bromide, into a rapidly agitated aqueous solution of a silver halide peptizer, preferably gelatin, a gelatin derivative or some other protein peptizer. The pH and the pAg employed in this type of procedure are interrelated. For example, changing one while maintaining the other constant at a given temperature can change the size frequency distribution of the silver halide grains which are formed. However, generally the temperature is about 30 to about 90 degrees C., the pH is up to about 9, preferably 4 or less, and the pAg is up to about 9.8.

In some instances, the photographic properties of the elements containing the blended emulsion according to this invention can be further improved by coating a layer containing a water-soluble halide adjacent the blended emulsion layer. Preferably the pAg of the silver halide layers of the final element is raised to a pAg of above about 9.0 by this technique to obtain improved photographic properties.

The process of this invention can also be extended to incorporate color couplers into the silver halide emulsion during the mixing step. The incorporation of couplers or coupler solvents in direct-positive emulsions of the type in which a silver halide grain has a water-insoluble silver salt center and an outer shell composed of a fogged water-insoluble silver salt that develops to silver without exposure, prepared in various ways such as those described in Berriman, U.S. Pat. 3,367,778 issued Feb. 6, 1968, improves incubation stability; especially improved is the $D_{max.}$ loss observed upon incubation, with no loss in speed; this improvement can be obtained when the emulsions are processed in black-and-white Elon-hydroquinone developers and color developers. A useful coupler solvent for incorporating couplers in silver halide emulsions is di-n-butyl phthalate and useful couplers are cyan amidophenol couplers such as those described in U.S. Pat. 2,895,826 and the combination of an amidophenol coupler and a phenolic cyan coupler of the type described in U.S. Pat. 2,474,293.

The invention can be further illustrated by the following examples.

EXAMPLE 1

A silver bromoiodide emulsion having an average grain size of about 0.4 micron is fogged to maximum density as described in Illingsworth, U.S. Pat. 3,501,307 isued Mar. 17, 1970. Similarly 4 fine-grained silver bromoiodide emulsions having an average grain size of about 0.2 micron are fogged to different sensitivities so as to obtain the desired exposure latitude when combined with the coarse-grained emulsion. The above melts are combined at the ratio of 48 parts of the fogged coarse-grained emulsion to 52 parts of the fine-grained emulsions. The combined melt after being held for 2 hours is coated on a polyester support at 300 mg. silver/ft.^{2} and 360 mg. gelatin/ft.^{2}. Over the emulsion layer is coated a gelatin layer at 82 mg. gelatin/ft.^{2}.

EXAMPLE 2

A fogged coarse-grained silver bromoiodide emulsion as described in Example 1 is prepared. Similarly 4 fogged fine-grained silver bromoiodide emulsions as described in Example 1 are combined and the two melts are mixed, as described in Collins et al., U.S. Pat. 2,912,343, at the same ratio as in Example 1 just prior to coating on a polyester support at 300 mg. silver/ft.^{2} and 360 mg. gelatin/ft.^{2}. Over the emulsion layer is coated a gelatin layer at 82 mg. gelatin/ft.^{2}.

The coated samples are exposed for 10 seconds on an Eastman 1B sensitometer to light from a tungsten source modulated by a continuous wedge and developed for 6 minutes in an Elon-hydroquinone developer. After the samples are fixed, washed and dried the following results are obtained.

Example No.	$D_{max.}$	Contrast	$D_{min.}$ for an exposure range of Log E=3.0
1	3.52	1.10	0.5
2	4.35	1.48	0.2

It can be readily seen from the above table that the procedure of mixing the coarse-grained and fine-grained emulsions just prior to coating results in a higher contrast, higher $D_{max.}$ and a lower $D_{min.}$ for a given exposure range.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinbefore and in the appended claims.

We claim:

1. In a method of making a photographic element having at least one layer containing a blend of fogged, direct-positive silver halide emulsion wherein the average grain size of at least two component fogged emulsions of the blend differs by at least 50%, which method comprises preparing the respective component fogged, silver halide emulsions, blending said component silver halide emulsions, coating said emulsion blend on a support and reducing the liquid content of the coated blend; the improvement which comprises (1) deferring the blending until just prior to coating, (2) coating said blend on a support within about 2 minutes after blending and (3) drying to less than 15% carrier liquid content within 30 minutes.

2. A method according to claim 1 wherein at least two component fogged emulsions of said blend differ by at least 100% in average size.

3. A process according to claim 1 wherein said component silver halide emulsions are each monodispersed, fogged, silver halide emulsions.

4. A process according to claim 3 wherein at least one of said component emnulsions has an average grain size of less than 2 microns.

5. A process according to claim 1 wherein said blend is coated on a support within at least 1 minute after mixing said component emulsions.

6. A process according to claim 1 wherein at least one of said component emulsions has an average grain size of at least 0.3 micron and at least one other component of the blend has an average size which differs by at least 50% in average size.

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