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SILVER HALIDE LAYERED PHOTOGRAPHIC ELEMENT OF DIFFERENT LIGHT SENSITIVE LAYERS

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ABSTRACT OF THE DISCLOSURE

This invention relates to a process for producing a photographic element comprising coating a silver halide layer with a pAg of below about 8.6 and coating adjacent said layer a layer comprising a water-soluble halide containing sufficient halide ions such that the pAg of the final emulsion layers of the element is within the range of about 9.0 to 10.0. In one aspect, this invention relates to a means for coating a blended, fine grain, direct-positive emulsion to achieve improved photographic properties.

This invention relates to new processes for preparing photographic elements and the elements produced thereby. In one aspect, this invention relates to a process for coating a blended silver halide emulsion which comprises silver halide grains of different sizes and coating a layer of a water-soluble halide adjacent thereto. In another aspect, this invention relates to a photographic element comprising a silver halide emulsion layer comprising a blend of silver halide grains of different sizes and a layer comprising a water-soluble halide adjacent thereto.

It is known in the art that water-soluble halides can be admixed with silver halides to provide improved photographic properties in the silver halide emulsion, such as in Litzerman, Belgian Pat. 695,363 issued Sept. 11, 1967 corresponding to U.S. Ser. No. 618,354 filed Feb. 24, 1967. Improved D_{max} and D_{min} can be obtained from this admixture in direct-positive emulsions. However, where a mixture of aliquot portions of silver halides of different grain sizes are blended before coating into a single layer, the addition of a water-soluble halide, which raises the pAg of the emulsion, also induces Ostwald ripening and a corresponding decrease in photographic properties of the blended emulsion. The problem is especialy noticeable where one component of the blend has an average grain size of at least 0.3 micron and at least one other component of the blend has an average grain size which differs by at least 50%.

We have now found that photographic elements having improved properties can be obtained by coating a layer containing a water-soluble halide adjacent or contiguous with a layer comprising a blend of aliquot portions of silver halide emulsion wherein each portion is of substantially different grain size. Thus, this process allows one to hold the respective silver halide blend or aliquot portions at a low pAg prior to coating and then achieve the necessary high pAg for good photographic properties, such as high D_{max} and low D_{min}, by coating a layer adjacent and preferably contiguous to the silver halide coating.

In one preferred embodiment, this invention relates to a process for preparing a photographic element which comprises coating over at least one side of a support a silver halide layer with a pAg below 8.6, preferably within the range of 8.2 to about 8.6, and coating adjacent to said first layer a second layer comprising a water-soluble halide containing sufficient halide ions such

that the pAg of the emulsion layers of the final element is above 9 and preferably within the range of about 9.0 to 10.0.

In a preferred embodiment, the silver halide layer comprises a blend of at least two monodispersed silver halide emulsion having substantially different grain sizes.

In another preferred embodiment, the silver halide layer comprises a blend of at least two monodispersed silver halide emulsions wherein the average grain size of the second emulsion is at least 50% greater, and more preferably 100% greater, than the average grain size of the first emulsion.

In another embodiment, a layer comprising a water-soluble halide is coated contiguous with a silver halide layer which comprises a blend of silver halide grains wherein the average grain size of at least one portion of the blend is at least 0.3 micron in diameter, preferably at least 20% of the emulsion, by weight, comprises grains having an average diameter at least 0.3 micron in size, and at least 20% of the emulsion by weight comprises grains having an average grain size at least 50% less than said portion above 0.3 micron.

In another preferred embodiment, at least one component of the blend has an average grain size of at least 0.3 micron, but the average grain size of each component part is less than 2 microns.

Generally, any suitable water-soluble halide salt can be used in the layer adjacent the silver halide layer. Typical useful halide salts include the ammonium, potassium, sodium, lithium, cadmium and strontium salts. In carrying out the processes of this invention, the water-soluble halide salt is coated in a layer either above or below the silver halide layer, but is preferably coated contiguous with the silver halide layer after said silver halide layer is coated. Generally, the water-soluble halide is coated in the overlayer to provide a ratio of from about .006 to about .100 mole per mole of silver in the next adjacent layer, and preferably from about .012 to about .050 mole per mole of silver.

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, pp. 94–122, or in chaper 2 of "The Theory of the Photographic Process," by Mees and Jones (1966), published by the MacMillian Co. The grain size can also be measured using the projected areas of the grains. When the grains are substantially uniform in shape, the size distribution can be expressed quite accurately as either projected area or diameter of the grain photomicrographs as described in the above reference.

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, blends of monodispersed silver halide emulsions are coated by this process to obtain the improved qualities achieved with monodispersed emulsions, but with the extended latitude obtained with mixed grain sizes. 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

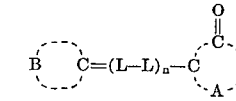
halide grains larger than the mean grain size, vary in diameter from the mean grain diameter by more than about 40%. Preferred direct-positive photographic emulsions of this invention comprise fogged silver halide grains, at least 95%, by weight, of said grains having a diameter or projected area which 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 Relations between Sensitometric and Size-Frequency Characteristics in Photographic Emulsion Series," in The Photographic Journal, vol. LXXIX, 1939, pp. 330–338. The aforementioned uniform size distribution of silver halide grains is a characteristic of the grains in "monodispersed" 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 a preferred embodiment, the silver halide layer comprises a blend of direct-positive, silver halide grains which have been fogged and which also contain electron acceptors and/or halogen conductors. The electron acceptors or halogen conductors which give particularly good results in the practice of this invention can be characterized in terms of their polarographic halfwave potentials, i.e., their oxidation reduction potentials determined by polarography. The electron acceptors useful herein have an anodic polarographic potential and a cathodic polarographic potential which, when added together, give a positive sum. The halogen conductors useful herein have an anodic polarographic potential less than 0.85 and a cathodic polarographic potential which is more negative than −1.0. Preferred halogen conductors have an anodic polarographic potential less than 0.62 and a cathodic polarographic potential which is more negative than −1.3. Cathodic measurements can be made with a 1×10^{-4} molar solution of the electron acceptor in a solvent, for example, methanol which is 0.05 molar in lithium chloride using a dropping mercury electrode with the polarographic halfwave potential for the most positive cathodic wave being designated E_c. Anodic measurements can be made with 1×10^{-4} molar aqueous solvent solution, for example, methanolic solutions of the electron acceptor which are 0.05 molar in sodium acetate and 0.005 molar in acetic acid using a carbon paste of pyrolytic graphite electrode, with the voltammetric half peak potential for the most negative anodic response being designated E_a. In each measurement, the reference electrode can be an aqueous silver—silver chloride (saturated potassium chloride) electrode at 20° C. Electrochemical measurements of this type are known in the art and are described in "New Instrumental Methods in Electrochemistry," by Delahay, Interscience Publishers, New York, 1954; "Polarography," by Kolthoff and Lingane, 2nd Edition, Interscience Publishers, New York, N.Y., 1952; "Analytical Chemistry, 36," 2426 (1964) by Elving; and "Analytical Chemistry, 30," 1576 (1958) by Adams. Signs are given according to IUPAC, Stockholm Convention 1953.

Advantageously, these electron acceptors used herein also provide spectral sensitization such that the ratio of minus blue relative speed to blue relative speed of the emulsion is greater than 7, and preferably greater than 10, when exposed to a tungsten light source through Wratten No. 16 and No. 35 plus 38A filters respectively. Such electron acceptors can be termed "spectrally sensitizing electron acceptors." However, electron acceptors can be used which do not spectrally sensitize the emulsion.

Typical good electron acceptor dyes used in direct-positive emulsions are disclosed in Illingsworth and Spencer, Belgian Pat. 695,364 granted Sept. 11, 1967 corresponding to U.S. Pat. 3,501,310 issued Mar. 17, 1970.

A preferred class of halogen-conducting compounds useful in this invention is characterized by an anodic halfwave potential which is less than 0.62 and a cathodic halfwave potential which is more negative than −1.3. A preferred class of halogen conductors that can be used in the practice of this invention comprises the spectral sensitizing merocyanine dyes having the formula:



where A represents the atoms necessary to complete an acid heterocyclic nucleus, e.g., rhodanine, 2-thiohydantoin and the like, B represents the atoms necessary to complete a basic nitrogen-containing heterocyclic nucleus, e.g., benzothiazole, naphthothiazole , benzoxazole and the like, each L represents a methine linkage, e.g.,

$$-CH=,\ -\underset{\displaystyle CH_3}{\underset{|}{C}}=\ \text{or}\ -\underset{\displaystyle C_6H_5}{\underset{|}{C}}=$$

and n is an integer from 0 to 2, i.e., 0, 1 or 2. Typical halogen-conducting compounds are disclosed in Wise, Belgian Pat. 695,361 granted Sept. 11, 1967.

In certain embodiments, improved results can also be obtained by deferring the mixing of the component emulsions to be blended until just prior to coating. In one aspect, this procedure is advisable when it is desirable to further prevent Ostwald ripening of the blended emulsion of different grain sizes.

This 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 issued 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 having an average grain size of 0.45 micron. 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 and the pAg raised to 9.5. 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 are treated as described in Example 1 and the 2 melts combined at the same ratio as in the previous example. The pAg of the combined melt is adjusted to 8.4, held for 2 hours, and coated on a polyester support at 300 mg. silver/ft.² and 360 mg. gelatin/ft.².

A melt, containing 454 gm. of gelatin dissolved in 4540 cc. of water, Saponin and 1300 cc. of a 3% aqueous solution of potassium bromide that raises the pAg to 10.0, is then coated at 82 mg. gelatin/ft.² over the emulsion layer.

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:

	$D_{max.}$	Contrast	$D_{min.}$ for an exposure range of log E=3.5
Example Number:			
1	3.68	1.0	.54
2	3.90	1.1	.38

It can be readily seen from the above table that the method of coating a high pAg gelatin layer over a lower pAg emulsion layer 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. A process for preparing a photographic element which comprises (1) coating on at least one side of a support a silver halide layer having a pAg below about 8.6 and which is a blend of at least two silver halide emulsions wherein one component emulsion of said blend comprises at least 20% of said emulsion blend, by weight, and has an average grain size at least 50% greater than another component emulsion which comprises at least another 20%, by weight, of said emulsion blend and (2) coating adjacent to said sliver halide layer and in association therewith a layer containing a water-soluble halide which will provide sufficient halide ions such that the pAg of said silver halide emulsion layer is above about 9.0.

2. A process according to claim **1** wherein said silver halide layer is coated at a pAg of from about 8.2 to about 8.6 and wherein the pAg of the silver halide emulsion layers of the final element is within the range of about 9.0 to 10.0.

3. A process according to claim **1** wherein said silver halide layer comprises a blend of direct-positive silver halide emulsions.

4. A process according to claim **1** wherein one of said component silver halide emulsions of said blend has an average silver halide grain size of at least 0.3 micron and the other said component emulsion has a silver halide grain size at least 50% smaller relative to said component part above 0.3 micron in size.

5. A process according to claim **1** wherein said silver halide emulsion is a fogged, direct-positive, silver halide emulsion which contains an electron acceptor which has an anodic polarographic halfwave potential and a cathodic halfwave potential which, when added together, give a positive sum.

6. A process according to claim **1** wherein said silver halide emulsion is a fogged, direct-positive, silver halide emulsion which contains a halogen-conducting compound which has an anodic polarographic potential less than 0.62 and a cathodic polarographic potential which is more negative than −1.3.

7. A process according to claim **1** wherein said water soluble halide is potassium bromide and is coated in a hydrophilic colloid layer.

8. A process according to claim **1** wherein said water-soluble halide is coated in said layer at a concentration of about .012 mole to about .050 mole per mole of silver in said adjacent layer.

9. A process according to claim **1** wherein said layer comprising said water-soluble halide is coated contiguous with said silver halide layer.

10. A process for preparing a photographic element which comprises (1) coating on at least one side of a support a silver halide layer having a pAg below about 8.6 and which is a blend of at least two chemically fogged, direct-positive, silver halide emulsions wherein one component emulsion of said blend comprises at least 20% of said emulsion blend, by weight, and has an average grain size at least 50% greater than another component emulsion which comprises at least another 20%, by weight, of said emulsion blend and (2) coating a layer comprising an alkali-metal or ammonium halide salt adjacent to said silver halide layer and in association therewith.

11. A photographic element which comprises (1) a support, (2) at least one layer which is a blend of at least two silver halide emulsions wherein one component emulsion of said blend comprises at least 20% of said emulsion blend, by weight, and has an average silver halide grain size at least 50% greater than another component emulsion which comprises at least another 20%, by weight, of said emulsion blend, and (3) a layer adjacent said silver halide layer and in association therewith which comprises a water-soluble halide.

12. A photographic element according to claim **11** wherein said sliver halide layer comprises a blend of monodispersed silver halide emulsions.

13. A photographic element according to claim **12** wherein said monodispersed silver halide emulsions are fogged, direct-positive emulsions.

14. A photographic element according to claim **12** wherein each component emulsion of said blend is a silver halide emulsion having an average grain diameter of less than about 2 microns.

15. A photographic element according to claim **11** wherein said silver halide emulsion comprises an electron acceptor which has an anodic polarographic halfwave potential and a cathodic halfwave potential which, when added together, give a positive sum.

16. A photographic element according to claim **11** wherein said silver halide emulsion comprises a halogen conductor which has an anodic polarographic potential less than 0.62 and a cathodic polarographic potential which is more negative than −1.3.

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96—94; 117—34