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# HAZE REDUCTION OF PHOTOGRAPHIC EMULSIONS CONTAINING A COVERING POWER AGENT

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This invention relates to photographic elements comprising a support coated with a gelatino silver halide emulsion containing an agent for increasing the covering power of the developed silver. This invention more particularly relates to such photographic elements having a transparent support. This invention, in a more particular aspect relates to a method of improving such photographic elements by improving the clarity and reducing the haze of the processed emulsion layers containing agents for increasing the covering power of the developed silver.

The use of covering power agents for developed silver in gelatino silver halide photographic emulsions is known. For example, in Jennings U.S. 3,063,838 there are disclosed and claimed gelatino-silver halide emulsions having increased silver covering power which contain 5 to 50% dextran based on the weight of total solids. It is also known to use poly-N-vinyllactams and certain other polymeric compounds for this purpose. As shown in the above patent, the presence of dextran in a gelatino-silver halide emulsion increases the efficiency of the developed silver in the processed element and manifests itself by increases in effective speed, contrast or gamma. The poly-N-vinyllactams, hydroxy alkyl ether starches, hydroxyalkyl polyvinyl ethers and certain polysaccharides also are effective in this role. Such increases in developed silver efficiency are much to be desired in certain types of photographic elements as for example, films for radiological use and also in the graphic arts field.

However, the use of such agents in gelatino-silver halide systems produces photographic emulsions which show a tendency toward turbidity or haziness in the coated and processed emulsion layer. This has the disadvantage in that it causes undesirable effects on clarity. This is particularly troublesome in radiological films used for diagnostic purposes, particularly when the films are viewed while still wet as is often done in this field.

It is an object of this invention to provide photographic elements coated on transparent supports which have reduced haze. A further object is to provide photographic elements, the emulsion layers of which contain silver covering power increasing agents, which are substantially free of haze. A still further object is to provide such elements which give images having increased clarity while still wet from processing. Other objects will appear hereinafter.

These and other objects are accomplished by the following invention which comprises a photographic emulsion containing a silver covering power increasing agent and containing an active amount of an alkali metal sulfate of ammonium sulfate. The presence of one or more of these sulfate salts markedly reduces the haze in films having developed gelatino-silver halide emulsion containing one of the above silver covering power increasing agents. The addition of the alkali metal or ammonium sulfates to the gelatino-silver halide emulsion containing the silver covering power increasing agent not only reduces haze to acceptable levels, but as a consequence increases the clarity of the developed images. The quantities of gelatin, silver halide and covering power agents used in a photographic emulsion are well known to one



skilled in the art. For example, the finished emulsion on a dry basis by weight could comprise about 1 to 25% covering power agent, about 20 to 70% gelatin, and 30 to 70% silver halide.

In general it has been found that the effective quantity of the sulfate salt may range from about 2 to 15 parts per 100 parts of gelatin. The sulfate salt may be added at any stage after the final washing step during the manufacture of the emulsion; but, preferably, it is added as a final addition just prior to coating. The sulfate salts are preferably added in an aqueous solution.

The haziness in the emulsion layers coated from emulsions containing the covering power increasing agents noted above is thought to be due to light scattering in the emulsion. This is believed to be caused by clumping of the gelatin molecules which are ionic in character and the covering power agent molecules which are polar in character because of ion-dipole interaction. The benefits obtained by using the covering power agents are outstanding; however, it is desirable to eliminate the haze problem when utilizing these agents. By adding ions which shield the charge and reduce the gelatin dextran attraction it is theorized that reduced haze results. While the above theory discloses the probable mechanism of this invention, it is presented as a theoretical explanation and the invention is not intended to be limited in any way by the above theory.

Haze may be determined by measuring the amount of loss (by scattering) of transmitted light through any particular photographic film or emulsion which contains a mixture of gelatin and a covering power agent. The silver halide of the emulsion or film is removed by fixation before the haze is measured. It is preferable to make the measurements on unexposed and undeveloped films because fog due to spontaneously developed silver also scatters light. For all practical purposes, the preferred method for making the measurement is the same as measuring a gelatin-covering power agent mixture in an emulsion or on a film when the mixture contains no silver halide grains. Therefore, while the haze will affect the quality of a photographic reproduction, the nature of the haze effect on a particular gelatin-silver halide emulsion containing a covering power agent can be determined by the haze effect on just a mixture of the gelatin and covering power agent.

The haze determinations in the following examples were made on undeveloped but fixed silver halide emulsion samples, on aqueous solutions of gelatin-covering power agent mixtures, and on coatings of gelatin-covering power agent mixtures having a coating weight equivalent to silver halide emulsion coatings.

The haze measuring instrument consists of a blue-filtered light source twenty-one inches from a photocell with micro ammeter; the light path is surrounded by a black tube except for an eight inch gap at the light source. Wet or dry films, or solutions in optical cells, are placed in this gap adjacent to the light source and haze is read as loss (by scattering) of transmitted light.

The invention will now be further illustrated by, but is not intended to be limited to the following examples. The quantities of covering power agent are given in grams based on the weight in grams of gelatin.

*Example I*

An X-ray type gelatino-silver iodobromide emulsion was made in the usual manner and digested with an organic sulfur compound and a gold salt. It contained approximately 1.6 mol percent of silver iodide and 98.4 mol percent of silver bromide. To the emusion after digestion there is added approximately 28 grams of dextran per 100 grams of gelatin. Dextran is a linear glucose polymer in which the units of one chain are in chemi-

cal union with members of adjacent chains to form a network structure. The main chain of the dextran polymer is made up of glucopyranose units in a 1,6-linkage with the side chain being a 1,4-linkage. The emulsion was then divided into two portions. To one portion there was added about 5 grams of sodium sulfate per 100 grams of gelatin. Both portions were coated and dried in the conventional manner .The films were then immersed in a conventional fixing solution (as described below) to remove the silver halide. Haze was then measured as described above to give the following results:

| | Haze |
|---|---|
| Control | 59 |
| Sample containing sodium sulfate | 50 |

The conventional solution used for fixation is prepared as follows:

| | | |
|---|---|---|
| Water | ml | 600 |
| Sodium thiosulfate (anhyd.) | grams | 15 |
| Sodium sulfite (anhyd.) | do | 18 |
| Potassium alum | do | 20 |
| Acetic acid (glacial) | ml | 12 |

Water to make, 1.0 liter.

The presence of sodium sulfate had no adverse effects on the sensitometric characteristics of the emulsion layer. A similar result is obtained when potassium sulfate is substituted for the above sodium sulfate.

*Example II*

An aqueous gelatin solution was made by disssolving 54 grams of gelatin in 506 grams of water. A second aqueous solution was made by dissolving in 506 grams of water, 54 grams of gelatin and 15 grams of dextran. A third solution was made by dissolving in 506 grams of water, 54 grams of gelatin, 15 grams of dextran and 3 grams of sodium sulfate. Haze measurements of the three solutions gave the following results:

| Solution No. | Composition | Haze |
|---|---|---|
| 1 | Water plus Gelatin | 62 |
| 2 | Water plus Gelatin plus Dextran | 137 |
| 3 | Water plus Gelatin plus Dextran plus Sodium Sulfate. | 69 |

The above solutions were coated on clear film base to a coating weight of 250 milligrams of silver bromide per square decimeter and haze measurements were made on samples which had been immersed in a fixing solution and washed and while still wet to give the following results:

| Coating No. | Composition | Haze |
|---|---|---|
| 1 | Water plus Gelatin | 7 |
| 2 | Water plus Gelatin plus Dextran | 92 |
| 3 | Water plus Gelatin plus Dextran plus Sodium Sulfate. | 58 |

The range of haze measurements (7 to 92) extends from a clear gelatin coating to the very hazy gelatin-dextran coating. The numbers are for comparison within a particular set; solution and coated film haze readings may not be inter-compared. It will be noted that sodium sulfate reduces gelatin-dextran solution haze almost to that of gelatin solution alone. The effect on wet haze of coated stock while not as large is still a substantial improvement over coatings containing no sodium sulfate. A similar result is obtained if ammonium sulfate is substituted above for sodium sulfate.

*Example III*

An aqueous solution was made by dissolving in 506 grams of water, 54 grams of gelatin and 15.1 grams of polyvinyl pyrrolidone having a molecular weight of approximately 45,000. This served as a control. A second solution was made by dissolving in 506 grams of water, 54 grams of gelatin, 15.1 grams of the above polyvinyl pyrrolidone and 3 grams of sodium sulfate. Haze determinations on solutions and coatings of the same weight as Example II gave the following results:

| Solution No. | Solution Haze | Haze of Wet Coatings |
|---|---|---|
| 1 (Control) | 144 | 90 |
| 2 | 64 | 8 |

It will be seen that the use of sodium sulfate decreases the haze to a considerable degree.

Developed silver images of reduced haze can be obtained in like manner by exposing the treated elements followed by developing and fixing the elements. The invention is not limited to gelatino-silver halide emulsions of the silver iodo-bromide type exemplified by Example I. This invention may be applied to other gelatino-silver halide emulsions, e.g., gelatino-silver bromochloride emulsions of the lithographic type. The invention is not limited to adding alkali metal and ammonium sulfates to gelatino-silver halide emulsions containing dextran and polyvinyl pyrrolidone as developed silver covering power increasing agents. Silver halide emulsions containing other covering power agents such as hydroxyalkyl ether starches, hydroxyalkyl polyvinyl ethers and certain polysaccharides are disclosed in assignee's patents, Chambers, U.S. 3,085,010, issued April 9, 1963; U.S. 3,085,009, issued April 9, 1963, and U.S. 3,087,818, issued April 30, 1963, and assignee's application, Chambers and Overman U.S. Ser. No. 66,442, filed November 1, 1960, now U.S. 3,137,575. The emulsions may contain any of the well known optical sensitizing dyes as well as nonoptical sensitizers such as sulfur sensitizers containing labile sulfur, e.g., allyl isothiocyanate, allyl diethyl thiourea, phenyl isothiocyanate, polyoxyalkylene ethers disclosed in Blake et al., U.S. Patent 2,400,532, and polyglycols disclosed in Blake et al., U.S. 2,423,549. Other nonoptical sensitizers such as amines as taught by Staud et al., U.S. Patent 1,925,508, and metal salts as taught by Baldsiefen, U.S. Patent 2,540,085, and Baldsiefen et al., U.S. Patent 2,540,086, may also be used. Antifoggants, e.g., benzotriazoles, triazaindenes and the phenolic antifoggants disclosed in Forsgard, U.S. Patent 3,043,697, may be used. Any of the usual film supports of macromolecular polymeric materials may be used such as cellulose esters, e.g., cellulose triacetate, cellulose acetate/butyrate; superpolymers, e.g., polystyrene, poly(vinyl chloride or vinyl acetate); polyvinyl acetals, e.g., formal and acetal; polyamides, e.g., polyhexamethylene adipamide, and polyesters, e.g., polyethylene terephthalate. The vinylidene chloride copolymer-coated oriented polyester films of Alles et al., U.S. Patent 2,627,088, are especially suitable.

The novel emulsion layers of this invention may be overcoated with heavy gelatin layers to further reduce the haze as taught in Meerkamper et al., U.S. 3,058,826.

An advantage of this invention is that the addition of alkali metal or ammonium sulfates to gelatino-silver halide emulsions containing developed silver covering power increasing agents provides a simple method of taking full advantage of the new discovery of using the above agents to improve maximum density, contrast and effective speed of the gelatino-silver halide emulsions.

Another advantage of the invention is that it provides a simple method of reducing haze in emulsions containing developed silver covering power increasing agents which may be carried out with conventional apparatus. Another advantage of the invention is that is provides a simple method of greatly increasing the clarity of the processed emulsion layers described above.

We claim:

1. In a process for preparing a gelatin-silver halide

emulsion containing a covering power agent where said mixture is coated on a film base the improvement which comprises adding to said emulsion about 2 to 15 parts 100 parts of gelatin of a compound selected from the group consisting of alkali metal sulfates and ammonium sulfate.

2. In a process for preparing a gelatin-silver halide emulsion containing the covering power agent dextran where said mixture is coated on a film base the improvement which comprises adding to said emulsion about 2 to 15 parts per 100 parts of gelatin of a compound selected from the group consisting of alkali metal sulfates and ammonium sulfate.

3. In a photographic emulsion containing gelatin, a silver halide and a covering power agent the improvement which comprises about 2 to 15 parts per 100 parts of gelatin of a compound selected from the group consisting of alkali metal sulfates and ammonium sulfate.

4. A photographic emulsion as described in claim 3 where said alkali metal sulfate is sodium sulfate.

5. A photographic emulsion as described in claim 3 where said alkali metal sulfate is potassium sulfate.

6. In a photographic emulsion containing gelatin, silver halide and dextran the improvement which comprises about 2 to 15 parts per 100 parts of gelatin of a compound selected from the group consisting of alkali metal sulfates and ammonium sulfate.

7. In a photographic emulsion containing gelatin, silver halide and polyvinyl pyrrolidone the improvement which comprises about 2 to 15 parts per 100 parts of gelatin of a compound selected from the group consisting of alkali metal sulfates and ammonium sulfate.



8. In a photographic emulsion containing about 20 to 70% by dry weight of gelatin, 30 to 70% by dry weight of silver halide and 1 to 25% by dry weight of a covering power agent the improvement which comprises 2 to 15 parts per 100 parts of gelatin of sodium sulfate.

9. In a photographic emulsion containing about 20 to 70% by dry weight of gelatin, 30 to 70% by dry weight of silver halide and 1 to 25% by dry weight of a covering power agent the improvement which comprises 2 to 15 parts per 100 parts of gelatin of potassium sulfate.

10. In a photographic emulsion containing about 20 to 70% by dry weight of gelatin, 30 to 70% by dry weight of silver halide and 1 to 25% by dry weight of a covering power agent the improvement which comprises 2 to 15 parts per 100 parts of gelatin of ammonium sulfate.

**References Cited by the Examiner**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,839,405 | 6/1958 | Jones | 96—107 |

**References Cited by the Applicant**

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,618,556 | 11/1952 | Hewitson et al. |
| 3,033,682 | 5/1962 | Hunt. |
| 3,063,838 | 11/1962 | Jennings. |

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