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GELATIN SILVER HALIDE COMPOSITIONS AND ELEMENTS CONTAINING A WATER-SOLUBLE HYDROXYALKYL ETHER DERIVATIVE OF STARCH

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No Drawing. Filed May 7, 1962, Ser. No. 193,653
15 Claims. (Cl. 96-94)

This invention relates to photographic compositions and to photographic elements including the same. More particularly, it relates to such compositions and elements having improved photographic characteristics, especially increased covering power of developed silver and improved maximum density, contrast and effective speed.

It is known to add certain chemical compounds, e.g., heavy metal and noble metal salts, to improve the sensitometric characteristics of photographic gelatino-silver halide emulsions. There is, however, at the present time, a practical limit to the advantages which can be obtained by the addition of such compounds without accompanying deleterious effects such as uncontrollable fog and instability on tropical aging.

It is also known to add to, or replace all or part of the gelatin in a gelatin-silver halide system with various polymeric colloid materials for various reasons including attempts to overcome the well-known disadvantages of gelatin. However, none of these proposed materials has overcome these disadvantages in a completely satisfactory manner, and gelatin is still used in most commercial photographic films. In general, when all of the gelatin is replaced by the synthetic polymers suggested by the prior art, the outstanding photographic and colloid-chemical properties of gelatin are lost. In addition, it is difficult to determine the optimum conditions for coating and drying, etc. to form a photographic element possessing satisfactory hardness and stability. This is particularly true when the exposed element contains the usual photographic hardeners and is placed in aqueous photographic processing solutions.

It is, therefore, an object of this invention to provide photographic compositions and elements having improved covering power of the developed silver. Another object is to provide such compositions and elements which also have improved maximum density, contrast and effective speed. A further object is to provide such improved compositions and elements wherein a part of the gelatin is replaced with a relatively inexpensive material. Yet another object is to provide such improved compositions and elements without an accompanying loss of other valuable properties. Other objects will appear hereinafter.

These and other objects are accomplished in accordance with this invention by the use of a photographic composition having improved covering power of developed silver comprising a gelatino-silver halide emulsion containing from about 20 to 80 parts by weight, preferably 30 to 70 parts, per 100 parts by weight of gelatin present in said emulsion, of a water-soluble hydroxyalkyl ether derivative of starch having an average molecular weight of from about 10,000 to 60,000 wherein from about 10 to 20% of the hydroxyl groups of said starch have been etherified to hydroxyl lower alkyl ether groups.

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In general, the above-described etherified starch derivative will constitute from about 5 to 50 percent and preferably from about 7 to 25 percent, by weight of total solids in the gelatino-silver halide emulsion. The emulsions may, of course, contain small amounts of conventional adjuvants.

The hydroxyalkyl ether derivatives of starch can be prepared by the general method of Hjermstad as set forth in Whistler, Industrial Gums, chapter XXXI, pp. 727-740 (Academic Press, New York, 1959). When the molecular weight of the starch derivative substantially exceeds 60,000 the material tends to become incompatible with gelatin. The hydroxyethyl and hydroxypropyl ether derivatives are particularly preferred.

Quite unexpectedly, it is found that the final emulsions of this invention have markedly increased covering power (e.g., 10 to 60% greater) over emulsions containing gelatin alone. More specifically, it is found that large increases in maximum density and contrast can be obtained in the developed image without any increase in the quantity of silver halide present. Covering power can be expressed as the numerical result of dividing optical density by the grams of silver per square decimeter in the developed image layer.

The covering power will, of course, vary with the amount of the etherified starch material used.

The invention is especially suited to photographic silver halide emulsions for radiological films, particularly those for medical diagnostic work. However, the invention is by no means limited to any particular type of photographic emulsion, and the etherified starch material may be utilized in any gelatino-silver halide system to improve its efficiency. The invention is also very useful in the so-called graphic arts films, i.e., lithographic films. In all cases when one of the hydroxyalkyl ethers of starch is present in the amounts set forth above, a higher density is obtained from a given amount of metallic silver in the developed photographic layer. Although the effect is more noticeable in large-grain emulsions, it is also effective in small-grain emulsions.

The methods of preparation of the compositions of this invention are quite simple, and consist of merely admixing with the molten or liquified emulsion after the digestion step, an aqueous solution of the hydroxyalkyl ether of starch. As an exemplary procedure, a gelatino-silver iodobromide emulsion is prepared by conventional methods. The silver halides are precipitated in gelatin and the resulting dispersion or emulsion ripened. The emulsion is then washed, either after chilling and noodling, or after coagulation by decanting the supernatant liquid. The emulsion is then redispersed and then it is digested to bring it to maximum speed. Following digestion, the esterified starch material (usually in aqueous solution) is added to the molten emulsion in an amount sufficient to provide the desired ratio of etherified starch to total solids. The usual final additions, e.g., of hardener, antifogging agents, sensitizing agents and spreading agents, are made and the emulsion is coated on a suitable support and dried in the usual manner. To test the effectiveness of the hydroxyalkyl ether of starch, the element is exposed in a sensitometer according to a procedure based on the "American Standard Method for the Sensitometry of Medical X-Ray Films PH2.9-1956."

The sensitometer used in the following examples was equipped with a neutral density $\sqrt{2}$ step wedge. The density of a selected step, as set forth in the tables, was measured and the quantity of metallic silver per square decimeter was determined by analysis. The density divided by the quantity of silver in grams per square decimeter was taken as a numerical expression of covering power.

The invention will now be further illustrated by, but is not intended to be limited to the following examples. The quantities of the etherified starch materials are given as parts per 100 parts of gelatin in the emulsion.

EXAMPLE I

A wheat starch is selected of which about 10-20% of the hydroxyl groups have been etherified with hydroxypropyl groups and a 10% aqueous solution of which has a viscosity at 25° C. of 25 cps, as measured by a Brookfield viscosimeter. An aqueous solution of the latter is added to a high speed gelatino-silver iodobromide emulsion which is made in the usual manner and digested with an organic sulfur compound and gold chloride. The emulsion contains approximately 1.6 mole percent of silver iodide and 98.4 mole percent of silver bromide. The emulsion is then divided into three portions and enough of the etherified starch material described above is added to each to give the parts per 100 parts of gelatin in the emulsion shown in the Table I below. An unaltered portion of the emulsion serves as a control. The emulsions are coated and dried in the conventional manner and the coatings are exposed in the sensitometer and developed for 5 minutes in a developer of the composition:

	Grams
p-N-methylaminophenol hydrosulfate	3
Anhydrous sodium sulfite	50
Hydroquinone	9
Anhydrous sodium carbonate	50
Potassium bromide	4.5
Water to make 1000.0 ml.	

Following development the films are fixed, washed and dried in the conventional manner. Representative results of sensitometric tests and measurements of covering power are shown in the following table:

Table I

Film No.	Parts of Starch Derivative per 100 Parts of Gelatin	Maximum Density	Covering Power at Maximum Density
1 (Control)	0	1.89	34
2	6	1.81	36
3	12	2.21	39
4	24	2.57	43

EXAMPLE II

Example I is repeated except that the etherified starch is added in an amount of 61 parts per 100 parts of gelatin to the silver iodobromide emulsion defined in Example I and coated and dried, exposed and processed as described therein with the following representative results:

Table II

Film No.	Parts of Starch Derivative per 100 Parts of Gelatin	Maximum Density	Covering Power at Maximum Density
1 (Control)	0	1.37	30
2	61	1.46	33

EXAMPLE III

The hydroxypropyl ether of starch described in Example I is added in the amounts set forth in Table III below to the gelatino-silver iodobromide emulsion made as described in Example I. The emulsions are coated and dried in the conventional manner and the coated films are exposed and processed as described above. The following results are representative:

Table III

Film No.	Parts of Starch Derivative per 100 Parts of Gelatin	Maximum Density	Covering Power at Maximum Density
1 (Control)	0	1.38	31
2	61	1.57	36
3	71	1.41	36
4	81	1.50	38

It has been found that the increased covering power of photographic emulsion layers is not limited to adding the above-described etherified starches to the gelatino-silver halide emulsion layer. It can be attained by incorporating the materials in a composition to be coated next to a gelatino-silver halide emulsion layer, e.g., in a gelatin sublayer, a separator or light-filtering layer or in an antiabrasion layer. The amount of etherified starch material so used can be based on the total gelatin in the contiguous layers. A layer essentially composed of one or a mixture of the hydroxyalkyl ethers of starch, e.g., 75% to 100% composition, can be used in a layer contiguous with a gelatino-silver halide emulsion layer.

The hydroxyalkyl ethers of starch are commercially available and may be obtained from the Hercules Powder Company, Wilmington, Delaware.

This invention is not limited to photographic gelatino-silver halide emulsions of silver iodobromide type; it may be applied to other gelatino-silver halide emulsions, e.g., gelatino-silver bromo-chloride emulsions of the lithographic type. The invention is particularly efficacious in photographic emulsions whose average grain size is relatively large. The emulsions may contain any of the well-known optical sensitizing dyes as well as non-optical sensitizers such as sulphur sensitizers, e.g., allyl isothiocyanate, allyl diethyl thiourea, phenyl isothiocyanate and sodium thiosulfate; the polyoxyalkylene ethers disclosed in U.S. Patent 2,400,532 and the polyglycols disclosed in U.S. Patent 2,423,549. Other non-optical sensitizers such as the amines disclosed in U.S. Patent 1,925,508 and the metal salts disclosed in U.S. Patents 2,540,085 and 2,540,086 may also be used. Antifoggants, e.g., benzothiazole and triazindenes can be used as well as the usual hardeners, i.e., chrome alum, formaldehyde, etc. The emulsions may be coated on any suitable support such as paper or films composed of cellulosic esters, e.g., cellulose triacetate, cellulose acetate/butyrate; superpolymers, e.g., vinyl chloride/vinyl acetate copolymers, polyvinyl acetals, e.g. formal and acetal; polystyrene; polyamides, e.g., polyhexamethylene adipamide, and polyesters, e.g., polyethylene terephthalate, polyethylene terephthalate/isophthalate and those polyesters obtainable by condensing terephthalic acid or dimethyl terephthalate with propylene glycol, diethylene glycol, tetramethylene glycol or cyclohexane - 1,4 - dimethanol (hexahydro - p - xylene alcohol). The vinylidene chloride copolymer-coated oriented polyesters films of U.S. Patents 2,627,086 and 2,779,684 are especially suitable.

An advantage of the invention is that it provides a simple, dependable and effective means for providing gelatino-silver halide photographic emulsions of enhanced covering power. The efficiency of the resulting developed silver is increased, that is, it can provide greater density per quantity of metallic silver which results from development.

Another advantage of the invention is that the addition of the hydroxyalkyl ethers of starch to photographic emulsions requires no special technique and can be carried out by the ordinary technician with conventional apparatus. Since the compounds are water soluble they can be added from an aqueous solution and they do not provide the problem of solvent recovery. Also, the resulting modified gelatino-silver halide emulsions can be coated and dried in the conventional coating and drying apparatus which offers commercial advantages. It is, therefore, apparent from the foregoing description of the invention that the objects thereof have been achieved as well as still further advantages apparent to those skilled in the art.

What is claimed is:

1. A photographic composition having improved covering power of developed silver comprising a gelatino-silver halide emulsion containing from about 20 to 80 parts by weight, per 100 parts by weight of gelatin present in said emulsion, of a water-soluble hydroxy-alkyl ether derivative of starch having an average molecular weight of from about 10,000 to 60,000 wherein from about 10 to 20% of the hydroxyl groups of said starch have been etherified to hydroxy lower alkyl ether groups.

2. A photographic composition according to claim 1 wherein said emulsion contains from about 30 to 70 parts of said water-soluble hydroxyalkyl ether derivative of starch per 100 parts of gelatin.

3. A photographic emulsion according to claim 1 wherein said hydroxy lower alkyl ether groups are hydroxypropyl ether groups.

4. A photographic emulsion according to claim 1 wherein said hydroxy lower alkyl ether groups are hydroxyethyl ether groups.

5. A photographic element having improved covering power of developed silver comprising a support layer and a gelatino-silver halide emulsion layer, said silver halide having in intimate contact therewith from about 20 to 80 parts by weight, per 100 parts of gelatin present in said element, of a water-soluble hydroxyalkyl ether derivative of starch having an average molecular weight of from about 10,000 to 60,000 wherein from about 10 to 20% of the hydroxyl groups of said starch have been etherified to hydroxy lower alkyl ether groups.

6. A photographic element having improved covering power of developed silver comprising a support layer and a gelatino-silver halide emulsion layer containing from about 20 to 80 parts by weight, per 100 parts of gelatin present in said element, of a water-soluble hydroxyalkyl ether derivative of starch having an average molecular weight of from about 10,000 to 60,000 wherein from about 10 to 20% of the hydroxyl groups of said starch have been etherified to hydroxy lower alkyl ether groups.

7. A photographic element having improved covering power of developed silver comprising a support layer, a gelatino-silver halide emulsion layer, and a gelatin-containing layer contiguous to said emulsion layer, said

gelatin-containing layer containing from about 20 to 80 parts by weight, per 100 parts of gelatin present in said element, of a water-soluble hydroxyalkyl ether derivative of starch having an average molecular weight of from about 10,000 to 60,000 wherein from about 10 to 20% of the hydroxyl groups of said starch have been etherified to hydroxy lower alkyl ether groups.

8. A photographic element according to claim 5 wherein the amount of said water-soluble hydroxy alkyl ether derivative of starch is from 30 to 70 parts per 100 parts of gelatin.

9. A photographic element according to claim 5 wherein said hydroxy lower alkyl ether groups are hydroxypropyl ether groups.

10. A photographic element according to claim 5 wherein said hydroxy lower alkyl ether groups are hydroxyethyl ether groups.

11. A process for preparing a gelatino-silver halide photographic composition having improved covering power of developed silver which comprises admixing with said composition from 20 to 80 parts per 100 parts of gelatin of a water-soluble hydroxyalkyl ether derivative of starch having an average molecular weight of from about 10,000 to 60,000 wherein from about 10 to 25% of the hydroxyl groups of said starch have been etherified to hydroxy lower alkyl ether groups.

12. A process for preparing a gelatino-silver halide photographic element of a gelatino-silver halide emulsion on a support whereby said element has improved covering power of developed silver which process comprises incorporating in intimate contact with said emulsion 20 to 80 parts per 100 parts of gelatin in said emulsion of a water-soluble hydroxyalkyl ether derivative of starch having an average molecular weight of from about 10,000 to 60,000 wherein from about 10 to 20% of the hydroxyl groups of said starch have been etherified to hydroxy lower alkyl ether groups.

13. A process according to claim 11 wherein the amount of said water-soluble hydroxy alkyl ether derivative of starch is from 30 to 70 parts per 100 parts of gelatin.

14. A process according to claim 11 wherein said hydroxy lower alkyl ether groups are hydroxypropyl ether groups.

15. A process according to claim 11 wherein said hydroxy lower alkyl ether groups are hydroxyethyl ether groups.

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**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,152,906

October 13, 1964

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 24, for "25%" read -- 20% --.

Signed and sealed this 9th day of March 1965.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

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