

UNITED STATES PATENT OFFICE

2,624,674

PHOTOGRAPHIC EMULSION SENSITIZED
WITH GOLD COMPOUNDS AND SULFUR
SENSITIZERS

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1

This invention relates to sensitized photo-
graphic emulsions and to a process for prepar-
ing the same.

Photographic silver halide emulsions prepared
in non-gelatin vehicles (or carrier) are, in gen-
eral, sensitized with sulfur compounds (i. e. sul-
fur sensitizers) with more difficulty than the
corresponding silver halide emulsions prepared
in gelatin.

We have now found, however, that non-gelatin
silver halide emulsions can be sensitized by add-
ing to the emulsions one or more soluble gold
compounds (i. e. one or more gold compounds
which provide gold ions in aqueous media) and
one or more sulfur sensitizers. The speed in-
creases caused by the combination of gold com-
pound and sulfur sensitizer in the non-gelatin
emulsions are at least equal to, and in some cases
very much greater than, the speed increases
which can be obtained employing a combina-
tion of gold compound and sulfur sensitizer in a
gelatino-silver-halide emulsion.

It is, accordingly, an object of our invention
to provide new photographic emulsions. A fur-
ther object is to provide a process for prepar-
ing such emulsions. Other objects will become
apparent hereinafter.

In accordance with our invention, we incor-
porate in a non-gelatin photographic silver hal-
ide emulsion, at any stage of its preparation, at
least one soluble gold compound and at least
one sulfur sensitizer. Our invention is directed
primarily to non-gelatin developing-out silver
halide emulsions in which the silver halide is
predominately silver bromide, i. e. silver hal-
ide emulsions in which the silver halide is wholly
silver bromide and silver bromide emulsions con-
taining smaller amounts of silver chloride or
silver iodide or both.

Among the non-gelatin silver halide emulsions
advantageously employed in practicing our in-
vention are silver halide emulsions prepared
using as the vehicle or carrier polyvinyl alcohol
("polyvinyl alcohol" is herein intended to in-
clude all water-soluble hydrolyzed polyvinyl
esters containing an ester group content equiv-
alent to from 0 to 5% by weight of polyvinyl
ester); silver halide emulsions prepared using
as the vehicle or carrier hydrolyzed polyvinyl
acetate containing an acetate group content
equivalent to from 59 to 71% by weight of
polyvinyl acetate; silver halide emulsions pre-
pared using as the vehicle or carrier polyvinyl
acetals containing a large proportion of polyvinyl
alcohol hydroxyl groups, e. g. polyvinyl acetal-

2

dehyde acetals containing polyvinyl acetaldehyde
acetal groups equivalent to at least 50% by
weight of polyvinyl acetaldehyde acetal and poly-
vinyl alcohol hydroxyl groups equivalent to at
least 15% by weight of polyvinyl alcohol, poly-
vinyl propionaldehyde acetals containing poly-
vinyl alcohol hydroxyl groups equivalent to from
45 to 60% by weight of polyvinyl alcohol, and
polyvinyl butyraldehyde acetals containing poly-
vinyl alcohol hydroxyl groups equivalent to from
60 to 80% by weight of polyvinyl alcohol, etc.
Any polyvinyl compound, especially those con-
taining only carbon, hydrogen and oxygen atoms,
or those containing carbon, hydrogen, oxygen
and amino nitrogen atoms or ammonium nitro-
gen atoms, which is soluble in a mixture of ethyl
alcohol and water (containing from 0 to 50%
by volume of ethyl alcohol) to the extent of 10
g. per 100 g. of solvent can be employed as the
vehicle or carrier in preparing our non-gelatin
silver halide emulsions. Moreover, any other
resinous or colloidal material soluble in an ethyl
alcohol-water mixture or in water, as stated
above, can be employed in preparing our non-
gelatin silver halide emulsions, e. g. soluble poly-
amide resins, such as described in United States
Patent 2,384,072, dated September 4, 1945, and
hydrolyzed copolymers of vinyl esters and eth-
ylene or propylene, such as described in United
States Patent 2,397,866, dated April 2, 1946. Still
further examples of colloidal materials which
can be employed as vehicles or carriers in prepar-
ing our non-gelatin emulsions are hydrolyzed cel-
lulose carboxylic esters, such as hydrolyzed cel-
lulose acetate or hydrolyzed cellulose acetate
propionate, containing from 19 to 33% by weight
of acyl groups, for example. Any cellulose com-
pound, especially those containing only carbon,
hydrogen and oxygen atoms, or those containing
only carbon, hydrogen, oxygen and amino nitro-
gen atoms or ammonium nitrogen atoms, which
is soluble in a mixture of ethyl alcohol and wa-
ter (containing from 0 to 50% by volume of
ethyl alcohol) to the extent of 10 g. per 100 g.
of solvent can be employed as the vehicle or car-
rier in preparing our non-gelatin silver halide
emulsions.

In connection with the non-gelatin colloidal
materials, such as polyvinyl alcohol, the silver
halide emulsions can be prepared using gelling
agents, such as phenols, e. g. orcinol, gallic acid,
2,4-dihydroxybenzoic acid, 4-chlororesorcinol, α -
naphthol, phloroglucinol, 2,7-dihydroxynaph-
thalene, etc. Moreover, the non-gelatin silver
halide emulsions can be prepared using silver

halide dispersing agents, e. g. starch acetate, gum arabic, a copolymer of maleic anhydride and vinyl acetate, low viscosity methyl cellulose, water-soluble amino carbohydrate dispersing agents (e. g. diethanolamine cellulose acetate or any other of these agents described in United States Patent 2,360,238, dated October 10, 1944), amino resin dispersing agents (e. g. dimethylaminobenzaldehyde acetals of polyvinyl alcohol, or water-soluble polyvinyl acetals in which at least a part of the acetal groups are 4-formylphenyltrialkylammonium salt acetal groups, such as the polyvinyl acetal of 4-formylphenyl trimethylammonium methylsulfate and other such compounds described in United States Patent 2,358,836, dated September 26, 1944), etc.

Polyvinyl compound silver halide emulsions and their preparation are described in United States Patents 2,286,215, dated June 16, 1942; 2,276,322, dated March 17, 1942; 2,276,323, dated March 17, 1942; 2,311,058, dated February 16, 1943; 2,311,059, dated February 16, 1943; 2,367,511, dated January 16, 1945; 2,376,371, dated May 22, 1945, and 2,110,491, dated March 8, 1938.

In non-gelatin silver halide emulsions where the colloidal material used as vehicle or carrier for the silver halide is a relatively poor protective colloid as is the case with the hydrolyzed cellulose carboxylic esters, the speeds obtained with the combination of gold salt and sulfur sensitizer are sometimes as great as ten times the speeds that can be obtained with sulfur sensitizers alone. Where the colloidal material is a relatively good protective colloid the speeds are more of the order of 3 to 4 times the speeds obtained with the sulfur sensitizers alone.

Typical soluble gold compounds which we employ in practicing our invention are gold halides, such as auric chloride, or complex gold halides, such as potassium auric chloride (KAuCl_4), auric sulfate, sodium auric chloride, potassium or sodium auric bromide, potassium or sodium auric iodide, complex gold salts, such as alkali metal aurous thiosulfates, alkali metal aurous sulfites, a complex salt formed by the interaction of thiourea and auric chloride, complex salts, such as gold thiosinamine complexes, etc. One or more gold compounds can be used.

The gold compound is advantageously employed in a concentration equal to from about 0.0005 to about 0.025% by moles of the silver halide present. Optimum results are obtained ordinarily at concentrations between about 0.001 and 0.02% by moles of the silver halide present.

The gold compounds can be added to the emulsions at any stage of their preparation. The gold compounds are advantageously incorporated in the emulsions in the form of their solutions in a suitable solvent such as water, methyl or ethyl alcohol.

Typical sulfur sensitizers which we employ in practicing our invention are sulfur compounds containing $>\text{C}=\text{S}$ groups and $-\text{S}-\text{S}-$ groups, e. g. thiourea, allyl isothiocyanate, thiosinamine, etc. Metal or ammonium thiocyanates, e. g. sodium, potassium, ammonium, cadmium, calcium, etc. thiocyanates can also be employed. One or more sulfur sensitizers can be employed, and one or more thiocyanates selected from the group consisting of metal and ammonium thiocyanates can be employed in conjunction with a sulfur sensitizer other than a thiocyanate containing a cation selected from the group consisting of metal and ammonium cations. The sulfur sensitizers are advantageously incorporated in the emulsions

in the form of their solutions in a suitable solvent, such as water, methyl or ethyl alcohol.

The sulfur sensitizers can be incorporated in the emulsions at any stage of the preparation of the emulsion, i. e. during precipitation of the silver halides, during washing of the emulsions or during digestion or heat treating of the emulsions. When incorporating thiocyanates in the emulsions prior to washing, the amount can vary widely. Advantageously, however, an amount of thiocyanate equal to from about 2 to about 15 per cent by moles of the silver halide in the emulsion is employed. If the thiocyanate or other sulfur sensitizer is not added until later in the preparation, e. g. after washing, it is advantageous to employ an amount equal to from about 0.1 to about 2.5 per cent by moles of the silver halide present in the emulsion in the case of metal and ammonium thiocyanates, and an amount equal to from about 0.006 to about 0.06 per cent by moles of the silver halide in the case of other sulfur sensitizers.

It is advantageous to digest, i. e. heat treat, the emulsion with both the gold compound and the sulfur sensitizer present. Depending upon whether or not the emulsions are prepared employing organic solvents which vaporize readily, the digestion can be carried out at from 90 to 150° F. for example. The lower the temperature of digestion, the longer it will require to arrive at optimum speed. Ordinarily at 120° F., digestion for from 1 to 2 hours produces optimum speed. During digestion, the pH of the emulsion is advantageously adjusted to the acid side of neutrality, e. g. between 5 and 6.5 for aqueous systems. Maintenance of the emulsion on the acid side of neutrality is also advantageous during coating.

The following examples will serve to illustrate further the manner of practicing our invention.

Example 1.—Polyvinyl alcohol emulsion

A polyvinyl alcohol silver bromiodide emulsion was prepared as follows:

40 g. of polyvinyl alcohol were dissolved in 2200 cc. of water and 200 cc. of concentrated ammonium hydroxide (about 28% ammonia) were added to the solution. The resulting solution was heated to 90° F. and solutions A and B (below) were allowed to run into it simultaneously with stirring over a 10-minute period.

| | | |
|---|--------------------------------------|----------------------|
| A | { 200 g. of silver nitrate..... | } Temperature 80° F. |
| | { Water to 400 cc. volume..... | |
| B | { 152.3 g. of potassium bromide..... | } Temperature 80° F. |
| | { 4.75 g. of potassium iodide..... | |
| | { Water to 400 cc. volume..... | |

To the resulting mixture were added 2500 cc. of a 10% (by weight) solution of polyvinyl alcohol in water. Then 200 cc. of glacial acetic acid were added. The resulting emulsion was heated to 140° F. and then 300 cc. of a 7% (by weight) solution of α -naphthol (gelling agent) in ethanol were added. The resulting emulsion was set by chilling. It was then shredded, washed with water and melted. The pH of the melted emulsion was adjusted to 5.5.

One-half of the melted emulsion was coated on a cellulose acetate film base in the usual manner. Upon exposure and development for 6 minutes at 70° F. in Eastman Kodak Company's "D-16" developer, the coated emulsion showed a speed (10/i) of 0.20, and a gamma of 1.5.

To the other half of the melted emulsion were added 800 mg. of sodium thiocyanate and 23 g. of KAuCl_4 . The emulsion was then heated for one hour at 120° F. and then coated on cellulose ace-

tate film base in the usual manner. On exposing and developing as above, this coated emulsion showed a speed (10/i) of 0.84 and a gamma of 1.28.

Example 2.—Hydrolyzed cellulose acetate propionate emulsion

A hydrolyzed cellulose acetate propionate silver bromide emulsion was prepared as follows:

40 g. of partially hydrolyzed cellulose acetate propionate (containing an acyl group content equivalent to about 23% by weight of acetyl) were dissolved in 2200 cc. of ethanol and 960 cc. of water, and the temperature of the solution was adjusted to 80° F. The following two solutions A and B were then allowed to run into the aforesaid solution simultaneously with stirring over a 20-minute interval:

| | | |
|------------------------------|------------------------------------|--------------------|
| A | 200 g. of silver nitrate..... | Temperature 80° F. |
| | Water to 400 cc. volume..... | |
| B | 152.3 g. of potassium bromide..... | Temperature 80° F. |
| | 4.75 g. of potassium iodide..... | |
| Water to 400 cc. volume..... | | |

To the resulting mixture were added 380 cc. of a 50% (by weight) solution of citric acid in water and 3200 cc. of a 10% (by weight) solution of partially hydrolyzed cellulose acetate propionate (acyl group content equivalent to about 23% by weight of acetyl) in a mixture of ethyl alcohol and water (equal volumes). The emulsion was precipitated by pouring the resulting solution into water with stirring. The precipitated emulsion was washed with water until free from ethyl alcohol. The washed emulsion was pressed to a weight of 2500 g. and the following solvents were added:

2500 cc. ethanol
400 cc. ethylene glycol diacetate

Upon heating, the emulsion dissolved in these solvents.

To one-half of this emulsion dispersion were added 40 mg. of 3-ethyl-5-(2-ethyl-1-benzothiazolyli-dene-2-thio-2,4(3,5)-oxazolidione and the resulting emulsion was coated on cellulose acetate film base in the usual manner. On exposure and 6 minutes' development in Eastman Kodak Company's "D-16" developer at 70° F., the coated emulsion showed a speed (10/i) of 1.40 and a gamma of 2.5.

To the other half of the emulsion dispersion were added 0.65 g. of sodium thiocyanate and 24 mg. of KAuCl₄ and the emulsion was heated for one hour at 120° F. 40 mg. of 3-ethyl-5-(2-ethyl-1-benzothiazolyli-dene-2-thio-2,4(3,5)-oxazolidione were then added and the emulsion was coated on cellulose acetate film base. On exposure and development as above, the coated emulsion showed a speed of 11.2 and a gamma of 2.5.

Example 3

5 g. of partially hydrolyzed cellulose acetate propionate (containing an acyl group content equivalent to about 23% by weight of acetyl) were dissolved in 160 cc. of water and 420 cc. of ethanol, and the temperature of the solution was adjusted to 80° F. 8 g. of urea and 2 cc. of concentrated ammonium hydroxide (28% ammonia) were added to this solution. The following two solutions A and B were then allowed to run into the aforesaid solution simultaneously with stirring over a 3-minute interval:

| | | |
|-----------------------------|---------------------------------|--------------------|
| A | 40 g. silver nitrate..... | Temperature 80° F. |
| | Water to 80 cc. volume..... | |
| B | 32 g. of potassium bromide..... | Temperature 80° F. |
| | 1 g. of potassium iodide..... | |
| Water to 80 cc. volume..... | | |

0.4 g. of sodium thiocyanate (in the form of a 10% (by weight) solution in water) were added to the resulting emulsion and the emulsion was held for 1 minute at 80° F. Then 62 cc. of a 50% (by weight) solution of citric acid in water were added, followed by 50 g. of cellulose acetate propionate (23% apparent acetyl) dissolved in 300 cc. of water and 300 cc. of acetone. The emulsion was precipitated by pouring the resulting solution into water with stirring. The precipitated emulsion was washed with water until free from organic solvents. It was then pressed to a weight of 360 g. and the following solvents added:

| | |
|--|-----|
| | cc. |
| Water | 440 |
| Acetone | 280 |
| Monoethyl ether of ethylene glycol | 200 |
| Monoacetin | 24 |

The resulting emulsion was then split into four equal parts of which three were treated as follows:

| | Amount of KAuCl ₄ added | |
|------------|------------------------------------|--------------------------|
| | Mg. | |
| No. 1..... | 0 | heated 1 hour, at 90° F. |
| No. 2..... | 0.1 | Do. |
| No. 3..... | 0.6 | Do. |

Then, 4 mg. of 3-ethyl-5-(2-ethyl-1-benzothiazolyli-dene-2-thio-2,4(3,5)-oxazolidione were added to each portion and then each portion was coated on cellulose acetate film. The coated emulsions on exposure and development for 6 minutes in Eastman Kodak Company's "D-16" developer at 70° F., showed the following results:

| | Speed (10/i) | Gamma | Fog |
|------------|--------------|-------|-----|
| No. 1..... | 1.4 | 2.2 | .06 |
| No. 2..... | 2.24 | 2.0 | .06 |
| No. 3..... | 4.4 | 1.8 | .08 |

Example 4

An emulsion was prepared as in Example 2. Instead of dividing the emulsion into halves and adding sodium thiocyanate and gold compound as in Example 2, portions of the emulsion were treated as follows:

| | Amount of emulsion | Amount of sodium thiocyanate | Amount of KAuCl ₄ | Time of heating |
|------------|--------------------|------------------------------|------------------------------|------------------------|
| | | Mg. | Mg. | |
| No. 1..... | 1/2 | 17 | 0.5 | 1 1/2 hours at 120° F. |
| No. 2..... | 1/2 | 35 | 0.5 | Do. |
| No. 3..... | 1/2 | 35 | 1.0 | Do. |
| No. 4..... | 1/2 | 35 | 1.0 | Do. |
| No. 5..... | 1/2 | 35 | 1.5 | Do. |

7 mg. of 3-ethyl-5-(2-ethyl-1-benzothiazolyli-dene-2-thio-2,4(3,5)-oxazolidione were then added to each portion of emulsion and then each portion of emulsion was coated on cellulose ace-

tate film. Upon exposure and developing as in Example 1, the following results were obtained:

| | Speed (10/i) | Gamma | Fog |
|------------|--------------|-------|------|
| No. 1..... | 0.82 | 2.4 | 0.03 |
| No. 2..... | 1.52 | 2.38 | 0.03 |
| No. 3..... | 2.05 | 2.24 | 0.05 |
| No. 4..... | 2.64 | 2.20 | 0.05 |
| No. 5..... | 3.72 | 2.20 | 0.06 |

Example 5

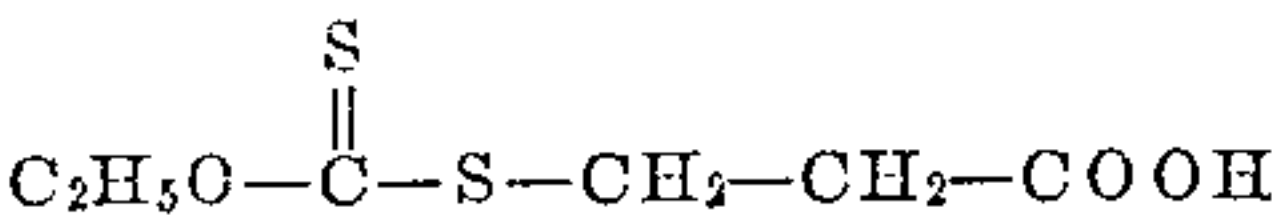
An emulsion was prepared as in Example 2. Instead of dividing the emulsion into halves and adding sodium thiocyanate and gold compound as in Example 2, portions of the emulsion were treated as follows:

| | Amount of emulsion | Amount of β -ethyl xanthate propionic acid | Amount of KAuCl_4 | Time of heating |
|------------|--------------------|--|----------------------------|--------------------|
| No. 1..... | $\frac{1}{12}$ | Mg. 0 | Mg. 0 | 2 hours at 120° F. |
| No. 2..... | $\frac{1}{12}$ | 2 | 1.0 | Do. |
| No. 3..... | $\frac{1}{12}$ | 7 | 3.5 | Do. |
| No. 4..... | $\frac{1}{12}$ | 10 | 5.0 | Do. |

7 mg. of 3-ethyl-5(2-ethyl-1-benzothiazolylidene-2-thio-2,4(3,5)-oxazolidione were then added to each portion of emulsion and then each portion of emulsion was coated on cellulose acetate film. Upon exposure and development as in Example 1, the following results were obtained:

| | Speed (10/i) | Gamma | Fog |
|------------|--------------|-------|------|
| No. 1..... | 1.18 | 2.4 | 0.02 |
| No. 2..... | 1.38 | 2.54 | 0.02 |
| No. 3..... | 3.90 | 1.91 | 0.01 |
| No. 4..... | 5.50 | 2.06 | 0.01 |

β -ethyl xanthate propionic acid employed as a sulfur sensitizer above has the following formula:



As pointed out above, non-gelatin silver halide emulsions do not respond to sensitization with sulfur sensitizers readily, and heretofore, it has been desirable to use silver halide dispersing agents such as water-soluble amino carbohydrate dispersing agents or water-soluble amino resin dispersing agents in order to arrive at sulfur sensitized non-gelatin silver halide emulsions having speeds paralleling those of gelatino-silver-halide emulsions. By means of our invention, however, non-gelatin silver halide emulsions of greatly enhanced sensitivity can be obtained without the use of the aforesaid dispersing agents, although our invention contemplates non-gelatin silver halide emulsions, sensitized as described herein, containing the aforesaid dispersing agents.

The thiocyanates which we have found are most advantageously employed in practicing our invention are the alkali metal thiocyanates, e. g. sodium or potassium thiocyanate, the alkaline earth metal thiocyanates, e. g. calcium thiocyanate, and the ammonium thiocyanates, e. g. NH_4SCN . Of course, thiocyanates containing cations which cations are known to have, in themselves, a deleterious effect on silver halide emulsions should be avoided. Otherwise the beneficial effects attained by our invention would be partially nullified by the deleterious action of the

cation. Thus, iron thiocyanate which contains the iron cation should be avoided.

Sensitizing dyes of all types can be employed to spectrally (optically) sensitize our new emulsions, e. g. erythrosin, Congo red, any of the sensitizing cyanine dyes (monomethine, trimethine, pentamethine, heptamethine, etc.), any of the sensitizing merocyanine dyes (see United States Patent 2,078,233, dated April 27, 1937, for example), any of the sensitizing hemicyanine dyes (see United States Patent 2,166,736, dated July 18, 1939, for example), any of the sensitizing hemioxonol dyes (see United States Patent 2,216,441, dated October 1, 1940, and United States Patent 2,165,339, dated July 11, 1939, for example), etc.

Photographic elements comprising our new emulsions can be made up in the usual manner by coating the flowable emulsions onto a support of a suitable material, such as glass, photographic paper, cellulose derivative or resin film, etc. to desired thickness, and then setting the coated emulsion.

Our new emulsions can contain hardening agents, setting agents, stabilizing agents, supersensitizing combinations of sensitizing dyes or a supersensitizing combination of one or more sensitizing dyes and another substance.

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

1. A photographic silver halide emulsion in which the carrier for the silver halide is a colloidal material selected from the group consisting of polyvinyl alcohol, hydrolyzed polyvinyl acetate containing an acetate group content equivalent to from 59 to 71 percent by weight of polyvinyl acetate, polyvinyl acetaldehyde acetals containing polyvinyl acetaldehyde acetal groups equivalent to at least 50 percent by weight of polyvinyl acetaldehyde acetal and polyvinyl alcohol hydroxyl groups equivalent to at least 15 percent by weight of polyvinyl alcohol, polyvinyl propionaldehyde acetals containing polyvinyl alcohol hydroxyl groups equivalent to from 45 to 60 percent by weight of polyvinyl alcohol, polyvinyl butyraldehyde acetals containing polyvinyl alcohol hydroxyl groups equivalent to from 60 to 80 percent by weight of polyvinyl alcohol and hydrolyzed cellulose carboxylic esters in which the acyl groups contain from 2 to 3 carbon atoms, said cellulose esters containing from 19 to 33 percent by weight of said acyl groups, sensitized with a soluble gold compound and a sulfur sensitizer, the concentration of the gold compound in the emulsion being equal to from about 0.0005 to about 0.025 per cent by mols of the silver halide present in the emulsion, and the concentration of the sulfur sensitizer being equal to about 0.006 to about 2.5 percent by mols of the silver halide present in the emulsion.

2. A photographic silver halide emulsion in which the silver halide is predominantly silver bromide and in which the carrier for the silver halide is polyvinyl alcohol, sensitized with a soluble gold compound and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates, the concentration of the gold compound in the emulsion being equal to from about 0.0005 to about 0.025 per cent by mols of the silver halide present in the emulsion, and the concentration of the thiocyanate being equal to from about 0.1 to about 2.5 percent by mols of the silver halide present in the emulsion.

9

3. A photographic silver halide emulsion in which the silver halide is predominantly silver bromide and in which the carrier for the silver halide is a hydrolyzed cellulose carboxylic ester in which the acyl groups contain from 2 to 3 carbon atoms, said cellulose ester containing from 19 to 33 percent by weight of said acyl groups, sensitized with a soluble gold compound and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates, the concentration of the gold compound in the emulsion being equal to from about 0.0005 to about 0.025 percent by mols of the silver halide present in the emulsion, and the concentration of the thiocyanate being equal to from about 0.1 to about 2.5 percent by mols of the silver halide present in the emulsion.

4. A photographic silver halide emulsion in which the silver halide is predominantly silver bromide and in which the carrier for the silver halide is a hydrolyzed cellulose acetate propionate containing from 19 to 33 percent by weight of acyl groups, sensitized with a soluble gold compound and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates, the concentration of the gold compound in the emulsion being equal to from about 0.0005 to about 0.025 percent by mols of the silver halide present in the emulsion, and the concentration of the thiocyanate being equal to from about 0.1 to about 2.5 percent by mols of the silver halide present in the emulsion.

5. A photographic silver halide emulsion in which the silver halide is predominantly silver bromide and in which the carrier for the silver halide is a hydrolyzed polyvinyl acetate containing an acetate group content equivalent to from 59 to 71 percent by weight of polyvinyl acetate, sensitized with a soluble gold compound and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates, the concentration of the gold compound in the emulsion being equal to from about 0.0005 to about 0.025 percent by mols of the silver halide present in the emulsion, and the concentration of the sulfur sensitizer being equal to from about 0.1 to about 2.5 percent by mols of the silver halide present in the emulsion.

6. A photographic silver halide emulsion in which the silver halide is predominantly silver bromide and in which the carrier for the silver halide is a polyvinyl acetaldehyde acetal containing polyvinyl acetaldehyde acetal groups equivalent to at least 50 percent by weight of polyvinyl acetaldehyde acetal and polyvinyl alcohol hydroxyl groups equivalent to at least 15 percent by weight of polyvinyl alcohol, sensitized with a soluble gold compound and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates, the concentration of the gold compound in the emulsion being equal to from 0.0005 to about 0.025 percent by mols of the silver halide present in the emulsion, and the concentration of the sulfur sensitizer being equal to from about 0.1 to about 2.5 percent by mols of the silver halide present in the emulsion.

7. A photographic silver halide emulsion in which the silver halide is predominantly silver bromide and in which the carrier for the silver halide is a polyvinyl propionaldehyde acetal containing polyvinyl alcohol hydroxyl groups equivalent to from 45 to 60 percent by weight of polyvinyl alcohol, sensitized with a soluble gold compound and a thiocyanate selected from the group

10

consisting of alkali metal and ammonium thiocyanates, the concentration of the gold compound in the emulsion being equal to from about 0.0005 to about 0.025 percent by mols of the silver halide present in the emulsion, and the concentration of the sulfur sensitizer being equal to from about 0.1 to about 2.5 percent by mols of the silver halide present in the emulsion.

8. In a process for preparing a sensitized photographic silver halide emulsion in which the carrier for the silver halide is a colloidal material selected from the group consisting of polyvinyl alcohol, hydrolyzed polyvinyl acetate containing an acetate group content equivalent to from 59 to 71 percent by weight of polyvinyl acetate, polyvinyl acetaldehyde acetals containing polyvinyl acetaldehyde acetal groups equivalent to at least 50 percent by weight of polyvinyl acetaldehyde acetal and polyvinyl alcohol hydroxyl groups equivalent to at least 15 percent by weight of polyvinyl alcohol, polyvinyl propionaldehyde acetals containing polyvinyl alcohol hydroxyl groups equivalent to 45 to 60 percent by weight of polyvinyl alcohol and polyvinyl butyraldehyde acetals containing polyvinyl alcohol hydroxyl groups equivalent to from 60 to 80 percent by weight of polyvinyl alcohol and hydrolyzed cellulose carboxylic esters in which the acyl groups contain from 2 to 3 carbon atoms, said cellulose ester containing from 19 to 33 percent by weight of said acyl groups, the step which comprises digesting the emulsion in the presence of a soluble gold compound and a sulfur sensitizer, the concentration of the gold compound in the emulsion being equal to from about 0.0005 to about 0.025 percent by mols of the silver halide present in the emulsion, and the concentration of the sulfur sensitizer being equal to from about 0.006 to about 2.5 percent by mols of the silver halide present in the emulsion.

9. In a process for preparing a sensitized photographic silver halide emulsion in which the silver halide is predominantly silver bromide and in which the carrier for the silver halide is polyvinyl alcohol, the step which comprises digesting the emulsion on the acid side of neutrality in the presence of a soluble gold compound and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates, the concentration of the gold compound in the emulsion being equal to from about 0.0005 to about 0.025 percent by mols of the silver halide present in the emulsion, and the concentration of the thiocyanate being equal to from about 0.1 to about 2.5 percent by mols of the silver halide present in the emulsion.

10. In a process for preparing a sensitized photographic silver halide emulsion in which the silver halide is predominantly silver bromide and in which the carrier for the silver halide is a hydrolyzed cellulose carboxylic ester in which the acyl groups contain from 2 to 3 carbon atoms, said cellulose ester containing from 19 to 33 percent by weight of said acyl groups, the step which comprises digesting the emulsion on the acid side of neutrality in the presence of a soluble gold compound and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates, the concentration of the gold compound in the emulsion being equal to from about 0.0005 to about 0.025 percent by mols of the silver halide present in the emulsion, and the concentration of the thiocyanate being equal to from about 0.1 to about 2.5 percent by mols of the silver halide present in the emulsion.

11

11. In a process for preparing a sensitized photographic silver halide emulsion in which the silver halide is predominantly silver bromide and in which the carrier for the silver halide is a hydrolyzed cellulose acetate propionate containing from 19 to 33 percent by weight of acyl groups, the step which comprises digesting the emulsion on the acid side of neutrality in the presence of a soluble gold compound and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates, the concentration of the gold compound in the emulsion being equal to from about 0.0005 to about 0.025 percent by mols of the silver halide present in the emulsion, and the concentration of the thiocyanate being equal to from about 0.1 to about 2.5 percent by mols of the silver halide present in the emulsion.

12. In a process for preparing a sensitized photographic silver halide emulsion in which the silver halide is predominantly silver bromide and in which the carrier for the silver halide is a hydrolyzed polyvinyl acetate containing an acetate group content equivalent to from 59 to 71 percent by weight of polyvinyl acetate, the step which comprises digesting the emulsion on the acid side of neutrality in the presence of a soluble gold compound and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates, the concentration of the gold compound in the emulsion being equal to from about 0.0005 to about 0.025 percent by mols of the silver halide present in the emulsion, and the concentration of the thiocyanate being equal to from about 0.1 to about 2.5 percent by mols of the silver halide present in the emulsion.

13. In a process for preparing a sensitized photographic silver halide emulsion in which the silver halide is predominantly silver bromide and in which the carrier for the silver halide is a polyvinyl acetaldehyde acetal containing polyvinyl acetaldehyde acetal groups equivalent to at least 50 percent by weight of polyvinyl acetaldehyde acetal and polyvinyl alcohol hydroxyl groups equivalent to at least 15 percent by weight of polyvinyl alcohol, the step which comprises digesting the emulsion on the acid side of neutrality in the presence of a soluble gold compound and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates, the concentration of the gold compound in

12

the emulsion being equal to from about 0.0005 to about 0.025 percent by mols of the silver halide present in the emulsion, and the concentration of the thiocyanate being equal to from about 0.1 to about 2.5 percent by mols of the silver halide present in the emulsion.

14. In a process for preparing a sensitized photographic silver halide emulsion in which the silver halide is predominantly silver bromide and in which the carrier for the silver halide is a polyvinyl propionaldehyde acetal containing polyvinyl alcohol hydroxyl groups equivalent to from 45 to 60 percent by weight of polyvinyl alcohol, the step which comprises digesting the emulsion on the acid side of neutrality in the presence of a soluble gold compound and a thiocyanate selected from the group consisting of alkali metal and ammonium thiocyanates, the concentration of the gold compound in the emulsion being equal to from about 0.0005 to about 0.025 percent by mols of the silver halide present in the emulsion, and the concentration of the thiocyanate being equal to from about 0.1 to about 2.5 percent by mols of the silver halide present in the emulsion.

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