

UNITED STATES PATENT OFFICE

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PHOTOGRAPHIC EMULSION

John A. Leermakers, Rochester, N. Y., assignor to
Eastman Kodak Company, Rochester, N. Y., a
corporation of New Jersey

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This invention relates to photographic emulsions and more particularly to photographic emulsions of the silver halide type.

It is known in the spectral sensitization of photographic silver halide emulsions by means of sensitizing dyes that the effectiveness of certain sensitizing dyes can be increased by employing them in combination with other sensitizing dyes. That is to say, with certain combinations of sensitizing dyes, the combined sensitization is substantially greater in some spectral region than is the sensitization produced by any one of the dyes in the absence of the other or others. The combined effect is not additive. This phenomenon has been termed "supersensitization." Instances of supersensitizing combinations of dyes are set forth in U. S. Patents 2,075,046, 2,075,047 and 2,075,048, each dated March 30, 1937.

I have now found that unusual supersensitizing effects can be obtained in silver halide emulsions by employing a mixture or a combination of a sensitizing dye with a metal thiocyanate and/or an ammonium thiocyanate. Such emulsions possess not only high speeds, but good keeping qualities and the other properties essential to a practical high speed emulsion, providing the concentration of the thiocyanate, with respect to the silver halide in the emulsion, lies within a certain range, as hereinafter set forth. My new method of supersensitizing spectrally (optically) sensitized emulsions is an improvement over the aforesaid known methods, since even the effect attained by a supersensitizing combination of two or more sensitizing dyes can be enhanced by my new method.

I am aware that such thiocyanates have been employed in photographic processes heretofore, but they have not heretofore been employed in the same manner in which I employ them, nor have they heretofore been employed for the same purpose. Thus, such thiocyanates have been added to finished emulsions in large quantities for the purpose of toning. For example, gelatino-silver-halide emulsions have been prepared, and, to the finished emulsions have been added amounts of thiocyanates equal to, roughly, 10% by moles of the silver halide in the emulsions. Such emulsions are said to be self-toning. Such emulsions, however, do not possess the characteristics, e. g. the higher speeds, of my new emulsions, and, rel-

ative to my new emulsions, possess inferior keeping qualities.

Contrasted with the foregoing processes, which always involve the addition of large quantities of thiocyanates to finished photographic emulsions for the purpose of securing toning effects, I prepare my new silver halide emulsions by incorporating in either a washed or unwashed silver halide emulsion, a sensitizing dye for the emulsion and a thiocyanate in an amount equal to not more than about 3% by moles of silver halide in the emulsion.

My new process and emulsions are not to be confused with those described in the copending application of Adolph H. Nietz and Frederick J. Russell, Serial No. 254,267, filed of even date herewith. Whereas they prepare emulsions in the presence of a thiocyanate, i. e. incorporate a thiocyanate in the emulsion at some stage during its preparation, I incorporate in the finished emulsion (either washed or unwashed) a thiocyanate in an amount as set forth above, together with a sensitizing dye. After preparing their emulsions in the presence of a thiocyanate, Nietz and Russell show that they may add sensitizing dyes and further show that the speed of their emulsions is substantially uniformly increased throughout the entire spectral region. Contrasted with their emulsions, my new emulsions, obtained by incorporating thiocyanates together with sensitizing dyes in the finished emulsions, do not possess substantially uniformly increased speed throughout the entire spectral region. Thus, in my new emulsions, prepared using alkali metal, alkaline earth metal or ammonium thiocyanates, there is little or no increase in speed in the violet and blue, i. e. in the region to which the emulsion is sensitive without addition of the sensitizing dye. Rather, in my new emulsions, the substantial increase in sensitivity occurs in that region for which the sensitizing dye sensitizes. Of course, in cases where the region to which the sensitizing dye sensitizes, overlaps with that region to which the emulsion is sensitive in the absence of the dye, my new emulsions do show increased sensitivity in the blue. Very frequently the spectral sensitivity curve of my new emulsions, obtained by adding thiocyanates to finished emulsions, is shifted so that there is a remarkable change in the sensitivity of one spec-

tral region relative to other spectral regions. Also, I have found that incorporation of thiocyanates in finished sensitized emulsions extends the region of sensitization produced by the dye to the red end of the spectrum, in some cases.

I have found that the effect produced by soluble thiocyanates, such as alkali metal thiocyanates, alkaline earth thiocyanates and ammonium thiocyanates is different from that produced by silver thiocyanate. In the first instance, silver thiocyanate, unlike the other thiocyanates, does sometimes produce an appreciable increase in sensitivity in the blue regardless of the region to which the dye sensitizes. In addition, the emulsions obtained by using silver thiocyanate possess better keeping qualities than the emulsions produced using the other thiocyanates.

It is an object of my invention, therefore, to provide novel and improved photographic emulsions. A further object is to provide a process for preparing such emulsions. Other objects will become apparent hereinafter.

According to my invention, I incorporate metal and/or ammonium thiocyanates in unwashed or washed, finished silver halide emulsions, together with sensitizing dyes. My invention is particularly directed to washed, finished emulsions, since it is not advantageous to employ some sensitizing dyes in unwashed emulsions. Furthermore, the effects obtainable according to my invention are much more pronounced in washed, finished emulsions. It is, of course, well known that silver halide emulsions can be prepared according to the following fundamental steps:

1. *Precipitation*, wherein the silver halide is precipitated by the interaction of a soluble silver salt and an excess of a soluble halide, in the presence of a carrier, such as gelatin.
2. *Digestion*, wherein the above precipitate is digested for a period of time at a raised temperature, e. g., 50-60° C., with or without the addition of further carrier.
3. *Washing*, wherein the ripened, solidified (e. g., by chilling) emulsion is washed with water to remove soluble salts.
4. *Melting-out and second digestion*, wherein the washed emulsion is heated for a period of time with or without the addition of further carrier, after which the emulsion is flowable.

Of course, variations of the above four steps can be employed. An emulsion, which is coated without washing, I call an unwashed, finished emulsion. An emulsion, which is coated after washing and melting-out, I call a washed, finished emulsion.

The thiocyanates which I have found are most advantageously employed in practicing my invention are the alkali metal thiocyanates, such as sodium or potassium thiocyanate for example, the alkaline earth metal thiocyanates, such as barium or calcium thiocyanate, for example, ammonium thiocyanate (NH_4SCN), and silver thiocyanate. Of course, thiocyanates containing cations, which cations are known to have, in themselves, a deleterious effect on the silver halide emulsions, should be avoided. Otherwise, the improvements attained by my invention would be partially nullified by the deleterious effect of the cation. The iron cation is, of course, one that would naturally be avoided in the manufacture of photographic silver halide emulsions and, therefore, in practicing my invention, iron thiocyanates should be avoided.

The water-soluble thiocyanates are advantageously incorporated in the emulsions in the form of their solutions in water, although they can be added in the solid form or in any other suitable solvent. Silver thiocyanate and other water-insoluble thiocyanates are advantageously incorporated in the emulsions in the form of a colloidal dispersion, i. e., dispersed in gelatin, gum arabic or the like. The thiocyanate can be added prior to, simultaneously with or after the addition of the sensitizing dye. The amount of thiocyanate added should not be more than about 3% by moles of the silver halides in the emulsion. With larger amounts, e. g., 5%, emulsions of high speed and practical keeping qualities are not obtained. I have found that about one-half to about two mole percent of thiocyanate (based on the silver halides in the emulsion) is advantageously employed. Smaller amounts can be employed, although, of course, as the concentration becomes very small, the beneficial effects are quite small. Generally speaking, the lowest practical concentration of thiocyanate is of the order of 0.05 mole percent.

As sensitizing dyes, I employ any of the known types and advantageously those which are not of a markedly acidic nature, i. e., those devoid of sulfonic acid (SO_3H), sulfinic acid (SO_2H), sulfuric acid (SO_4H) and carboxylic acid (COOH) groups and their metallic and ammonium salt forms, e. g., COONa or COONH_4 . Advantageously, I employ sensitizing dyes from the cyanine, merocyanine, hemicyanine and hemioxonol classes of dyes which are devoid of the aforesaid acidic groups and their metal and ammonium salt forms. A number of sensitizing cyanine dyes are, of course, well known substances. Sensitizing merocyanine dyes are described, for example, in United States Patent 2,078,233, dated April 27, 1937. Sensitizing hemicyanine dyes are described, for example, in the copending application of Frank L. White and Grafton H. Keyes, Serial No. 138,634, filed April 23, 1937. Sensitizing hemioxonol dyes are described, for example, in the copending application of Grafton H. Keyes, Serial No. 146,425, filed June 4, 1937. Another group of hemioxonol dyes is described in the copending application of Leslie G. S. Brooker, Serial No. 101,105, filed September 16, 1936.

The sensitizing dyes can be employed in various concentrations depending upon the effects desired. As is well known in the art, the sensitivity conferred upon an emulsion by a sensitizing dye does not increase proportionately to the concentration of the dye in the emulsion, but rather passes through a maximum as the concentration is increased. The dyes can be employed in the optimum concentration or in concentrations greater or less than the optimum. The optimum concentration of a sensitizing dye can be determined in a manner well known in the art by measuring the sensitivity of a series of emulsions containing different concentrations of the sensitizing dye. Ordinarily, the optimum or near optimum concentration is of the order of 5 to 20 mg. of the dye per liter of emulsion.

The sensitizing dyes are advantageously added to the emulsion in the form of their solutions in suitable solvents. Methyl alcohol suffices as a solvent for most sensitizing dyes. Acetone is frequently a satisfactory solvent for those dyes having a very limited solubility in methyl alcohol. Both the sensitizing dyes and the thiocya-

nate should be thoroughly dispersed throughout the emulsions.

My invention is particularly directed to the ordinary employed gelatino-silver-halide emulsions and more particularly to the gelatino-silver-bromide emulsions customarily employed in the art. The effects obtained in bromide and bromiodide emulsions are especially valuable. My invention can be employed with silver halide emulsions in which the carrier is other than gelatin, for example, a resinous substance or cellulosic derivative which has substantially no deleterious effect on the light-sensitive materials in the emulsion.

While my invention is subject to variation, particularly as respects the nature and quantity of the thiocyanate employed, the nature and quantity of sensitizing dye employed, the type of silver halide emulsion employed and the manner of incorporating the thiocyanates and sensitizing dyes in the emulsions, the following examples will serve to illustrate the manner of practicing my invention.

Example 1.—To an ordinary washed, finished, flowable gelatino-silver bromiodide emulsion made by the ammonia process and containing 10 grams of silver halides were added 10 cc. of a 0.1 N aqueous solution of sodium thiocyanate with stirring. To the resulting emulsion, 4 mg. of 2,2'-diethyl-8-methylthiacarbocyanine iodide, dissolved in methyl alcohol, were added, with stirring. The resulting emulsion possessed a red sensitivity, as measured through a Wratten No. 25 filter, 50% greater than that of the same emulsion sensitized with the same concentration of 2,2'-diethyl-8-methylthiacarbocyanine iodide, but not containing a thiocyanate.

Example 2.—To an ordinary washed, finished, flowable gelatino-silver-bromiodide emulsion made by the ammonia process and containing 10 grams of silver halides were added 5 cc. of a 0.1 N aqueous solution of ammonium thiocyanate, with stirring. To the resulting emulsion, 2 mg. of 3-ethyl-5-[(2-ethyl-1(2)-benzoxazylidene) ethylidene] rhodanine were added with stirring. The resulting emulsion possessed a green sensitivity, as measured through a Wratten No. 58 filter, 100% greater than that of the same emulsion sensitized with the same concentration of 3-ethyl-5-[(2-ethyl-1(2)-benzoxazylidene) ethylidene] rhodanine, but not containing a thiocyanate.

Example 3.—To an ordinary washed, finished, flowable gelatino-silver-chloriodide emulsion containing 205 grams of silver halides were added 0.4 g. of finely powdered potassium thiocyanate, with stirring. To the resulting emulsion were added, with stirring, 0.1 gram of 2,2'-diethyl-8-methyl-3,4,3',4'-dibenzothiacarbocyanine chloride dissolved in methyl alcohol. The resulting emulsion possessed a sensitivity to white light about 25% greater than that of the same emulsion sensitized with the same concentration of 2,2'-diethyl-8-methyl-3,4,3',4'-dibenzothiacarbocyanine chloride. The red sensitivity, as measured through a Wratten No. 25 filter, was about 100% greater.

Example 4.—To about 400 cc. of an ordinary washed, finished, flowable gelatino-silver-bromiodide emulsion containing 10 grams of silver halides was added an aqueous solution containing 80 mg. of calcium thiocyanate. The concentration of the calcium thiocyanate in the resulting emulsion was equal to 0.8 percent by moles of the silver halides. To the resulting emulsion were added, with stirring, 4 mg. of 2-[4-(1-piperidyl)- $\Delta^{1,3}$ -

butadienyl]- β -naphthothiazole ethiodide. The resulting emulsion possessed a green sensitivity, as measured through a Wratten No. 58 filter, 40% greater than that of the same emulsion sensitized with the same concentration of 2-[4-(1-piperidyl)- $\Delta^{1,3}$ -butadienyl]- β -naphthothiazole ethiodide, but not containing any thiocyanate.

Example 5.—To about one liter of an ordinary washed, finished, flowable gelatino-silver-bromiodide emulsion were added, simultaneously and with stirring, an aqueous solution of sodium thiocyanate (containing an amount of sodium thiocyanate equal to about one percent by moles of the silver halides in the emulsion) and a methyl alcoholic solution containing about 10 mg. of 2,2'-diethyl-8-methyl-3,4,3',4'-dibenzothiacarbocyanine chloride. The resulting emulsion possessed a red sensitivity, as measured through a Wratten No. 25 filter, 40% greater than that of the same emulsion sensitized with the same concentration of 2,2'-diethyl-8-methyl-3,4,3',4'-dibenzothiacarbocyanine chloride, but not containing any thiocyanate.

Example 6.—A suspension of silver thiocyanate was prepared as follows: three solutions, A, B and C, were prepared in the following manner.

- A. 100 g. of photographic gelatin were dissolved in 2000 cc. of water at a temperature of 50° to 60° C. The temperature was then lowered to about 25° C. and 10 g. of silver nitrate dissolved in 20 cc. of water were slowly added with stirring.
- B. 220 g. of sodium thiocyanate were dissolved in 600 cc. of water.
- C. 400 g. of silver nitrate were dissolved in 2400 cc. of water.

All three solutions were brought to a temperature of about 25° C. Then, solutions B and C were simultaneously, slowly added, with stirring, to solution A. Silver thiocyanate precipitated to give a suspension. 400 g. of photographic gelatin were dissolved in the suspension, at about 50° C. The suspension was then chilled for several hours to set it. It was then shredded and washed with water for three-quarters of an hour to remove soluble thiocyanates.

To an ordinary washed, finished, flowable gelatino-silver-bromiodide emulsion containing 10 g. grams of silver halides were added, with stirring, an amount of the above silver thiocyanate suspension containing 0.1 gram of silver thiocyanate. To the resulting emulsion were added, with stirring, a methyl alcoholic solution of 4 mg. of 2-[4-(1-piperidyl)- $\Delta^{1,3}$ -butadienyl]- β -naphthothiazole ethiodide. The resulting emulsion possessed a green sensitivity, as measured through a Wratten No. 58 filter, 100% greater than the same emulsion sensitized with the same concentration of 2-[4-(1-piperidyl)- $\Delta^{1,3}$ -butadienyl]- β -naphthothiazole ethiodide, but not containing any silver thiocyanate.

Still further examples of the preparation of my new emulsions could be given, but the foregoing are believed to demonstrate the manner of practicing my invention.

Photographic elements comprising my new emulsions can be made up in the usual manner by coating the flowable emulsions on to a support of a suitable material, such as glass, photographic paper, cellulose derivative or resin for example, to the desired thickness, and then drying the coated emulsion.

The following table contains a summary of

some of the more practical effects I have obtained according to my invention.

wherein A represents hydrogen or a C_nH_{2n+1} group wherein n represents a positive integer not

Table

Emulsion	Sensitizing dye		Thiocyanate		Percent increase in speed owing to thiocyanate			
	Name	Concentration in mg. per liter of emulsion	Formula	Concentration in mole per cent of silver halide	Clear	Blue ¹	Green ²	Red ³
1. Gelatino-silver-bromide.	2,2'-diethyl-8-methyl-3,4,3',4'-dibenzothiacarbocyanine chloride.	10	NaSCN...	1.7	+40	+25	-40	+80
2. Gelatino-silver chloride.	do.	5	NaSCN...	2.0	+40	-50	+80	+100
3. Gelatino-silver chlorobromide.	do.	20	NaSCN...	0.5	+40	0	+40	+40
4. Gelatino-silver-bromide.	do.	20	AgSCN...	1.5	+40	+40	+40	+80
5. Gelatino-silver-bromide.	2,2'-dimethyl-8-ethyl-3,4,3',4'-dibenzothiacarbocyanine iodide.	10	NaSCN...	1.7	+40	+40	-20	+40
6. Gelatino-silver-bromide.	2,2'-diethyl-8-methyl-3,4,3',4'-dibenzothiacarbocyanine iodide, and 2,2'-dimethyl-8-ethylthiacarbocyanine iodide.	12	NaSCN...	1.7	0	+50	-20	+50
7. Gelatino-silver-bromide.	3-ethyl-5[(2-ethyl-1(2)-benzoxazylidene) ethylidene] rhodanine.	10	NaSCN...	1.7	+80	+120	+150	0
8. Gelatino-silver-bromide.	do.	10	AgSCN...	0.5	+40	+40	+40	0
9. Gelatino-silver-bromide.	2[4-(1-piperidyl)-Δ ^{1,3} -butadienyl]-β-naphthothiazoleth iodide.	20	NaSCN...	1.7	+100	+100	+40	0
10. Gelatino-silver-bromide.	do.	10	AgSCN...	0.5	+40	+40	+100	+150
11. Gelatino-silver-bromide.	3-ethyl-5-[γ-(1-piperidyl) allylidene] rhodanine.	10	AgSCN...	0.5	+40	+70	+40	0
12. Gelatino-silver-bromide.	3-ethyl-5-(2-ethyl-1(2)-benzoxazylidene) ethylidene] rhodanine.	10	NH ⁴ SCN...	1.5	+40	+80	+100	0
13. Gelatino-silver-bromide.	2,2'-diethyl-8-methyl-3,4,3',4'-dibenzothiacarbocyanine bromide.	20	Ca(SCN) ₂	1.2	0	+25	-75	+120
14. Gelatino-silver-bromide.	2,2'-diethyl-8-methyl-3,4,3',4'-dibenzothiacarbocyanine chloride.	20	Cd(SCN) ₂	1.2	+25	+25	+25	+150

¹As measured through a Wratten No. 47 filter.

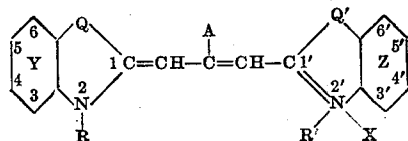
²As measured through a Wratten No. 58 filter.

³As measured through a Wratten No. 25 filter.

The considerable increases in speed that can be attained according to my invention are apparent from the above table. Under (1) in the above table, an ordinary gelatino-silver-bromide emulsion sensitized with 2,2'-diethyl-8-methyl-3,4,3',4'-dibenzothiacarbocyanine chloride, owing to the sodium thiocyanate, has increased in blue speed by about twenty-five percent, and decreased in green speed by about forty percent, while increasing in red speed by about eighty percent. Thus, by means of sodium thiocyanate, a remarkable increase in the red region relative to the green region has been effected. Under (2) in the above table, the relative change in sensitivity of the red and green regions is even more remarkable. In this case, the red speed has been increased to 100 percent, while the green speed has been decreased eighty percent. In this case, the region of sensitization has been definitely extended toward the longer wavelengths of light.

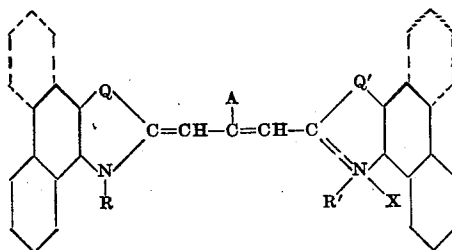
I have obtained particularly useful emulsions from sodium, potassium, ammonium, calcium and silver thiocyanates with ordinary gelatino-silver-bromide, bromide chloride and chlorobromide emulsions sensitized with sensitizing dyes from the following groups of dyes:

I. Carbocyanine dyes having the following general formula:



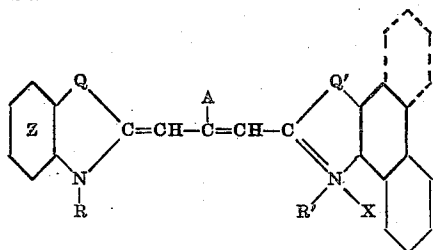
greater than five, Q and Q' represent oxygen, sulfur or selenium, R and R' represent C_nH_{2n+1} groups wherein n represents a positive integer, X represents an acid radical, preferably halide, and wherein the nuclei Y and Z may carry simple substituents, such as chlorine atoms and alkyl groups, for example.

II. Carbocyanines of the following general formula:



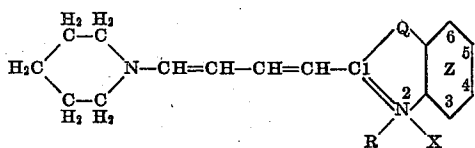
wherein A represents hydrogen or a C_nH_{2n+1} group wherein n represents a positive integer not greater than five, Q and Q' represent oxygen or sulfur, R and R' represent a C_nH_{2n+1} group wherein n represents a positive integer not greater than five, and X represents an acid radical, preferably halide.

III. Carbocyanines of the following general formula:



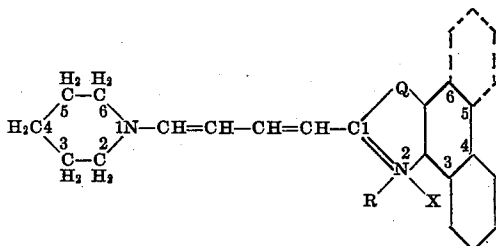
wherein A represents hydrogen or a C_nH_{2n+1} group wherein n represents a positive integer not greater than five, Q and Q' represent oxygen or sulfur, R and R' represent a C_nH_{2n+1} group wherein n represents a positive integer not greater than five, X represents an acid radical, preferably halide, and wherein the nucleus Z may carry simple substituents, such as chlorine atoms or alkyl groups, for example.

IV. Hemidicarbocyanines of the following general formula:



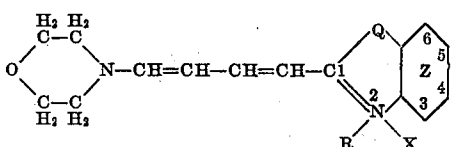
wherein Q represents oxygen, sulfur or selenium, R represents a C_nH_{2n+1} group wherein n represents a positive integer not greater than five, X represents an acid radical, preferably halide, and wherein the nucleus Z may carry simple substituents, such as chlorine atoms or alkyl groups, for example.

V. Hemidicarbocyanines of the following general formula:



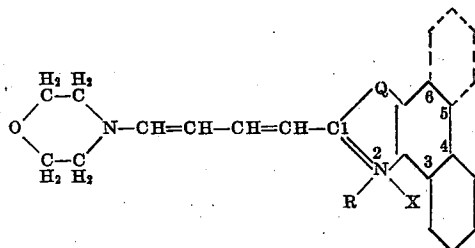
wherein Q represents oxygen or sulfur, and R and X have the values set forth above under IV.

VI. Hemidicarbocyanines of the following general formula:



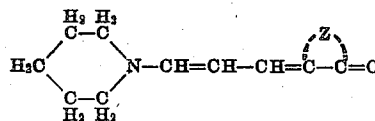
wherein Q, R, X and Z have the values set forth above under IV.

VII. Hemidicarbocyanines of the following general formula:



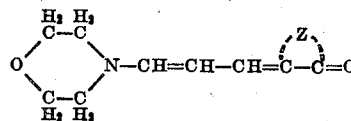
wherein Q, R and X have the values set forth under V above.

VIII. Hemicarboxonols of the following general formula:



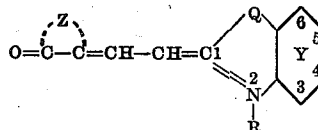
wherein Z represents the non-metallic atoms necessary to complete a rhodanine nucleus, a 3-alkyl-2,4(3,5)-oxazolidione nucleus, a 2-thiohydantoin nucleus, a 2-diphenylamino-4(5)-thiazolone nucleus or a 1-benzothiazyl-3-methyl-5-pyrazolone nucleus.

IX. Hemicarboxonols of the following general formula:



wherein Z has the value given under VIII above.

X. Merocarbocyanines of the following general formula:



wherein R represents a C_nH_{2n+1} group wherein n represents a positive integer not greater than five, Q represents oxygen, sulfur or selenium and Z has the values set forth under VIII above and the nucleus Y may carry simple substituents, such as chlorine atoms or alkyl groups.

I determine the sensitivity of emulsions in the usual manner, first coating the prepared emulsion on a glass plate to suitable thickness and drying the coated emulsion. The resulting photographic plate is then tested by means of a wedge spectrograph and a sensitometer, whereby spectral sensitivity and speed of the emulsion on the plate is determined.

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

1. A photographic silver halide emulsion containing a sensitizing dye for the emulsion and a thiocyanate selected from the group consisting of ammonium thiocyanates and metal thiocyanates, said thiocyanate having been introduced into the finished emulsion in a concentration equal to not more than about three percent by moles of the silver halide in the emulsion.

2. A photographic gelatino-silver-halide emulsion containing a sensitizing dye for the emulsion and a thiocyanate selected from the group consisting of ammonium thiocyanates and metal thiocyanates, said thiocyanate having been introduced into the finished emulsion in a concentration equal to not more than about three percent by moles of the silver halide in the emulsion.

3. A photographic gelatino-silver-halide emulsion containing a sensitizing dye for the emulsion and a thiocyanate selected from the group consisting of ammonium thiocyanates and metal thiocyanates which do not contain a cation which has a deleterious effect on the emulsion, said thiocyanate having been introduced into the finished emulsion in a concentration equal to from about one-half percent by moles of the silver halide in the emulsion to about two percent.

4. A photographic gelatino-silver-bromide emulsion containing a sensitizing dye for the emulsion and a thiocyanate selected from the group consisting of ammonium thiocyanates and metal thiocyanates which do not contain a cation which has a deleterious effect on the emulsion, said thiocyanate having been introduced into the finished emulsion in a concentration equal to not more than about three percent by moles of the silver bromide in the emulsion.
5. A photographic gelatino-silver-bromide emulsion containing a sensitizing dye for the emulsion and a thiocyanate selected from the group consisting of ammonium thiocyanates and metal thiocyanates which do not contain a cation which has a deleterious effect on the emulsion, said thiocyanate having been introduced into the finished emulsion in a concentration equal to from about one-half to about two percent by moles of the silver bromide in the emulsion.
6. A photographic gelatino-silver-halide emulsion containing a sensitizing dye for the emulsion and an alkali metal thiocyanate, said thiocyanate having been introduced into the washed, finished emulsion in a concentration equal to not more than about three percent by moles of the silver halide in the emulsion.
7. A photographic gelatino-silver-halide emulsion containing a sensitizing dye for the emulsion and an ammonium thiocyanate, said thiocyanate having been introduced into the washed, finished emulsion in a concentration of not more than about three percent by moles of the silver halide in the emulsion.
8. A photographic gelatino-silver-halide emulsion containing a sensitizing dye for the emulsion and silver thiocyanate, said silver thiocyanate having been introduced into the washed, finished emulsion in a concentration of not more than about three percent by moles of the silver halide in the emulsion.
9. A photographic gelatino-silver-halide emulsion containing a sensitizing dye for the emulsion, said dye being selected from the group consisting of cyanine dyes, merocyanine dyes, hemicyanine dyes and hemioxonol dyes which are devoid of sulfonic, sulfinic, sulfuric and carboxylic acid groups and the metal and ammonium salt forms of the said acid groups, said emulsion also containing a thiocyanate selected from the group consisting of metal and ammonium thiocyanates, said thiocyanate having been incorporated in the finished emulsion in a concentration equal to not more than about three percent by moles of the silver halide in the emulsion.
10. A photographic gelatino-silver-halide emulsion containing a sensitizing dye for the emulsion, said dye being selected from the group consisting of cyanine dyes, merocyanine dyes, hemicyanine dyes, and hemioxonol dyes which are devoid of sulfonic, sulfinic, sulfuric and carboxylic acid groups, said emulsion also containing silver thiocyanate, said thiocyanate having been introduced into the finished emulsion in a concentration equal to not more than about three percent by moles of the silver halide in the emulsion.
11. A photographic silver halide emulsion containing a sensitizing dye for the emulsion and a thiocyanate selected from the group consisting of ammonium and metal thiocyanates, said thiocyanate having been incorporated in the finished emulsion in a concentration equal to from about 0.05 to about 3 per cent by moles of the silver halide in the emulsion.
12. A photographic gelatino-silver-halide emulsion containing a sensitizing dye for the emulsion and a thiocyanate selected from the group consisting of ammonium and metal thiocyanates, said thiocyanate having been incorporated in the finished emulsion in a concentration equal to from about 0.05 to about 3 per cent by moles of the silver halide in the emulsion.
13. A photographic gelatino-silver-halide emulsion containing a sensitizing dye for the emulsion, said dye being devoid of sulfonic, sulfinic, sulfuric and carboxylic acid groups and the metal and ammonium salt forms of said acid groups, said emulsion also containing a thiocyanate selected from the group consisting of metal and ammonium thiocyanates which do not contain a cation which has a deleterious effect on the emulsion, said thiocyanate having been incorporated in the finished emulsion in a concentration of from about 0.05 to about 3 per cent by moles of the silver halide in the emulsion.
14. A photographic gelatino-silver-halide emulsion containing a sensitizing dye for the emulsion, said dye being selected from the group consisting of cyanine dyes, merocyanine dyes, hemicyanine dyes and hemioxonol dyes which are devoid of sulfonic, sulfinic, sulfuric and carboxylic acid groups and the metal and ammonium salt forms of said acid groups, said emulsion also containing a thiocyanate selected from the group consisting of metal and ammonium thiocyanates, said thiocyanate having been incorporated in the finished emulsion in a concentration equal to from about 0.05 to about 3 per cent by moles of the silver halide in the emulsion.
15. A photographic gelatino-silver-halide emulsion containing a sensitizing dye for the emulsion, said dye being selected from the group consisting of cyanine dyes, merocyanine dyes, hemicyanine dyes, and hemioxonol dyes which are devoid of sulfonic, sulfinic, sulfuric and carboxylic acid groups and the metal and ammonium salt forms of said acid groups, said emulsion also containing silver thiocyanate, said thiocyanate having been incorporated in the finished emulsion in a concentration equal to from about 0.05 to about 3 per cent by moles of the silver halide in the emulsion.

JOHN A. LEERMAKERS.