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SENSITIZATION OF PHOTOGRAPHIC SILVER HALIDE EMULSIONS WITH SULFUR-CONTAINING POLYMERS

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11 Claims. (Cl. 96—108)

This invention relates to photographic silver halide emulsions, and more particularly, to an improved means for sensitizing photographic silver halide emulsions with certain sulfur-containing polymers.

A number of methods have been previously described for increasing the sensitivity of photographic silver halide emulsions, other than methods of optical or spectral sensitization which involve the incorporation of certain colored compounds or dyes in the emulsions. The incorporation of such dyes in the emulsions increases the optical range of sensitivity, and for this reason such dyes are commonly referred to as optical or spectral sensitizing dyes. It is also well known to increase the sensitivity of photographic emulsions by addition of sulfur compounds capable of reacting with silver salts to form silver sulfide, or with reducing agents (compounds of these types are also naturally present in gelatin), or with salts of gold or other noble metals, or with combinations of two or more of the aforementioned compounds generally known as chemical sensitizers. Such chemical sensitizers are believed to react with the silver halide to form, on the surface of the silver halide, minute amounts of silver sulfide or of silver or of other noble metals, and these processes are capable of increasing the sensitivity of developing-out emulsions by very large factors. The process of chemical sensitization, however, reaches a definite limit beyond which further addition of sensitizer, or of further digestion with the sensitizer present, merely increases the fog of the photographic emulsion with constant or decreasing speed.

I have now found a means of further increasing the sensitivity of photographic emulsions which may be applied even though the ordinary processes of chemical sensitization have been carried to the effective limit of the photographic emulsion in question. My process is to be distinguished from hypersensitization, which is produced by bathing a finished coating with water or with solutions of ammonia, amines or silver salts. Such processes act primarily on optically sensitized photographic emulsions and tend to increase the free silver ion concentration of the emulsion and greatly diminish its stability. My process is also to be distinguished from hypersensitization by mercury vapor, which gives a transitory effect which is lost on storage of the film. The compounds used in my invention do not appear to be chemical sensitizers in the usual sense, since they increase speed by their presence during exposure and processing and required no digestion with the photographic emulsion to produce the increase in speed, nor does their chemistry indicate that they are likely to react with silver halide under normal emulsion conditions.

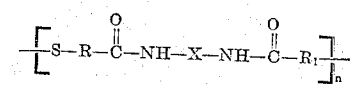
The novel sensitizers of my invention are quite unique in that the effects produced are additive in photographic emulsions which have already been sensitized to their optimum, or near-optimum, with conventional chemical sensitizers, such as labile sulfur compounds. The novel sensitizers of my invention, however, can be used to sensitize photographic silver halide emulsions containing no other sensitizers, if desired. The novel sensitizers of my invention are not strictly chemical sensitizers, since chemical sensitizers do not generally provide the additive effects of the type mentioned.

It is, therefore, an object of my invention to provide photographic silver halide emulsions which have been sensitized with certain polymeric compounds containing a plurality of sulfur atoms. Still another object of my invention is to provide photographic silver halide emulsions which have increased sensitivity of the type commonly attributed to chemical sensitization, but without concomitant increases in fog and/or poor keeping qualities, to a degree which might seriously affect the usefulness of the emulsions. Another object of my invention is to provide a new class of sulfur-containing polymers and methods for making them. Other objects will become apparent from a consideration of the following description and examples.

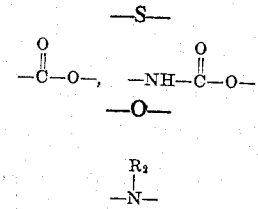
According to my invention, I have found that the sensitivity of an ordinary photographic silver halide emulsion can be materially increased by incorporating therein polymeric carboxylic amide compounds containing a plurality of thioether sulfur atoms, without prohibitively increasing fog in the emulsions. The polymeric compounds of my invention contain the aforementioned thioether linkages, by which I mean a linkage wherein the sulfur atom is a divalent atom which is joined to two carbon atoms. However, my invention also includes solubilized or ternarized derivatives of these thioether polymers. Such ternarized derivatives can be obtained by merely heating together (to fusion) the thiopolymer and an alkyl ester, such as methyl benzenesulfonate, methyl p-toluenesulfonate, ethyl sulfate, methyl sulfate, etc. My invention does not contemplate polyamide compounds containing disulfide linkages, such as those commonly found in vulcanized, rubbery materials. Moreover, the polymeric compounds of my invention are linear polymeric materials wherein the thioether sulfur atoms are present in the polymeric chain, as contrasted with polymeric materials containing their sulfur atoms as substituents on the chain, or as parts of a cross-linked arrangement. The polymeric materials used in my invention should have sufficient dispersibility in water (or a dilute alkaline solution), or an organic solvent, such as acetone, the lower alcohols, 1,4-dioxane, ethyl acetate, etc. (directly, or in a colloid mill, or by other means, such as by a dispersing agent, e.g., sodium laurylsulfate, etc.), so that a sensitizing amount of the polymeric materials can be adsorbed by or associated with the silver halide grains.

The linear polyamides of my invention, containing a plurality of thioether-sulfur atoms in the chain, include linear polymers which can advantageously be represented by the following general formula:

(I)



wherein R and R_1 each represents an alkylene group, e.g., methylene, ethylene, trimethylene, 1,2-propylene, butylene, etc. (especially alkylene groups containing from 1 to 4 carbon atoms), X represents an alkylene chain, such as ethylene, trimethylene, hexamethylene, decamethylene, etc., as well as alkylene chains containing in the chain a linkage such as the following:



or

wherein R_2 represents a hydrogen atom or a lower alkyl

group, such as methyl, ethyl, n-propyl, etc., and *n* represents an integer of at least about 2. In general, the linear polyamides of my invention have a molecular weight of at least about 350, although polymeric materials having a molecular weight of about 500 to 10,000 have been found to be particularly useful in my invention. The terminal groups of the polymers, represented by the above general Formula I, will vary depending upon the particular method used to prepare the polymers. In general, the terminal groups can be carboxyl groups, amino groups, mercapto groups, and the like.

The linear polyamides of my invention represented by Formula I above can advantageously be obtained by condensing together a mercaptocarboxylic acid, such as an acid selected from the class represented by the following general formula:

(II) $HS-R-\overset{O}{\overset{\|}{C}}-OH$

wherein R has the values given above, with a primary diamine, such as a diamine selected from the class represented by the following general formula:

(III) $H_2N-X-NH_2$

wherein X has the values given above. The ratio of the mercaptocarboxylic acid to diamine can be varied, although it will be noted that the reaction requires two molecules of mercaptocarboxylic acid for each molecule of diamine. The condensations can advantageously be carried out in the presence of an acid condensing agent, such as benzenesulfonic acid, p-toluenesulfonic acid, etc. The condensation can also be carried out in the presence of a solvent, such as toluene, p-xylene, and the like. Heat accelerates the condensations and generally it is advantageous to use sufficient heat to remove water from the reaction mixture by means of an azeotrope with the xylene or other water-immiscible solvent.

Instead of reacting one of the monocarboxylic acids of Formula II with one of the diamines of Formula III, it has been found that the linear polyamides of Formula I above can be prepared by condensing together a dibasic acid, such as an acid selected from the class represented by the following general formula:

(IV) $HO-\overset{O}{\overset{\|}{C}}-R-S-R_1-\overset{O}{\overset{\|}{C}}-OH$

wherein R and R_1 each have the values given above, with one molecule of a diamine selected from those represented by Formula III above. The same reaction conditions can advantageously be employed, namely, the use of an acid condensing agent, a water-immiscible solvent for removal of the by-product water by means of an azeotrope, and the application of heat. It is immediately apparent that a mixture of diamines and/or dibasic acids and/or mercaptocarboxylic acids can be employed to provide mixed polyamide compounds which are useful in sensitizing photographic silver halide emulsions.

Other linear polyamide compounds which are useful in practicing my invention can be prepared by condensing together a molecule of a dibasic acid, such as an acid selected from the class represented by the following general formula:

(V) $HO-\overset{O}{\overset{\|}{C}}-(R)_{m-1}-\overset{O}{\overset{\|}{C}}-OH$

m=1 or 2

wherein R has the values given above, with a diamine, such as a diamine of Formula III above, provided that the diamine has a thioether sulfur atom in the chain. In general, polymers obtained from the intermediates of Formula III and those of Formula V can be prepared according to the methods described above.

Typical acids embraced by Formulas II and IV include the following:

$HS-CH_2-COOH$
$HS-(CH_2)_2-COOH$
$HS-(CH_2)_3-COOH$
$HOOC-(CH_2)_2-S-(CH_2)_2-COOH$
$HOOC-(CH_2)_2-S-(CH_2)_2-S-(CH_2)_2-COOH$
$HOOC-(CH_2)_3-S-(CH_2)_3-COOH$

Typical acids employed by Formula V include dicarboxylic acids, such as succinic acid, glutaric acid, adipic acid, pimelic acid, sebacic aid, oxalic aid, etc.

Typical diamines employed by Formula III above include the following:

$H_2N-(CH_2)_5-NH_2$
$H_2N-(CH_2)_{10}-NH_2$
$H_2N-(CH_2)_3-O-(CH_2)_2-O-(CH_2)_3-NH_2$
$H_2N-(CH_2)_2-S-(CH_2)_2-NH_2$
$H_2N-(CH_2)_3-O-(CH_2)_3-NH_2$

$$H_2N-(CH_2)_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{N}}-(CH_2)_3-NH_2$$

$H_2N-(CH_2)_6-NH_2$
$H_2N-(CH_2)_2-S-(CH_2)_2-S-(CH_2)_2-S-(CH_2)_2-NH_2$
$H_2N-(CH_2)_3-S-(CH_2)_3-NH_2$

The linear polyamide compounds produced by condensing an intermediate selected from the class represented by Formula III above with a dibasic acid, such as those represented by Formula V above, can advantageously be represented by the following general formula:

(VI) $-\left[(R)_{m-1}-\overset{O}{\overset{\|}{C}}-NH-(R_1-S)_d-R_3-NH\overset{O}{\overset{\|}{C}}\right]_n-$

wherein R, R_1, *m* and *n* each have the values given above, R_3 represents an alkylene group, such as those listed above for R_1 (R_1 and R_3 can be identical or different from one another) and *d* represents a positive integer of from 1 to 3.

The following examples will serve to illustrate more fully the preparation of various linear polyamides containing thioether atoms which can be effectively used to sensitize photographic silver halide emulsions according to my invention.

EXAMPLE 1

Poly(4,15-Diaza-8,11-Dioxa-3,16-Dioxo-1-Thiaheptadecane)

$$2HS(CH_2)COOH+NH_2(CH_2)_3O(CH_2)_2O(CH_2)_3NH_2\longrightarrow$$

$$-\left[SCH_2\overset{O}{\overset{\|}{C}}NH(CH_2)_3O(CH_2)_2O(CH_2)_3NHCOCH_2\right]_{n(ca.3.5)}-+2H_2O+H_2S$$

Nine and two-tenths grams (0.10 mole) of mercaptoacetic acid, 8.8 grams of 4,7-dioxa-1,10-diaminodecane (0.05 mole) and 0.5 gram of p-toluenesulfonic acid were heated to reflux with 250 ml. of p-xylene while stirring vigorously. Water was azeotroped from the reaction mixture and collected in a Dean-Stark trap. After 7½ hours, 2 ml. of water (theory 1.8 ml.) had been collected. A test for the evolution of hydrogen sulfide with lead acetate paper was positive.

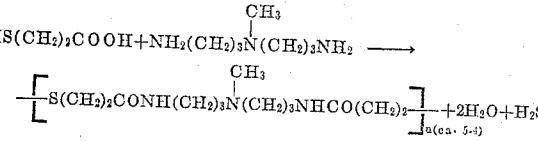
The excess p-xylene was distilled under vacuum leaving an orange oil. This oil was dissolved in 100 ml. of ethanol, filtered, chilled, and ether slowly added precipitating an orange viscous syrup weighing 12.7 g. (yield 88%).

Analysis.—Calcd. for $(C_{12}H_{22}N_2O_4S)_n$: C, 49.6; H, 7.6; N, 9.7; S, 11.0. Found: C, 48.9; H, 7.6; N, 9.5; S, 12.4.

A molecular weight determination on the syrup in ethanol showed the molecular weight to be approximately 1000.

EXAMPLE 2

Poly(4,14-Dioxo-9-Methyl-1-Thia-5,9,13-Triazahexadecane)



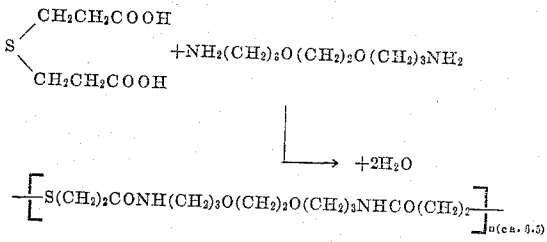
β-Mercaptopropionic acid (21.2 g., 0.20 mole), 14.5 g. of N-methyl-bis-aminopropylamine (0.10 mole), 0.5 g. of p-toluenesulfonic acid catalyst, and 250 ml. of p-xylene were heated to reflux with vigorous stirring. The water azeotroped from the p-xylene was collected in a Dean-Stark trap. After 14 hours, 2.6 ml. of water (theory 3.6 ml.) had been collected. The p-xylene was removed leaving a tan, viscous syrup which was dissolved in N,N-dimethylformamide, filtered and chilled while slowly adding ether. An orange oil was precipitated. Three attempts at recrystallization of the syrup gave 18.3 g. (64%) of a viscous tacky syrup.

Analysis.—Calcd. for $(C_{13}H_{25}N_3O_2S)_n$: C, 54.3; H, 8.7; N, 14.6; S, 11.0. Found: C, 52.5; H, 8.5; N, 13.2; S, 9.5.

A molecular weight determination from ethanol gave an average molecular weight of approximately 1735.

EXAMPLE 3

Poly(5,16-Diaza-9,12-Dioxa-4,17-Dioxo-1-Thianonadecane)



Thiodipropionic acid (8.9 g.) (0.05 mole), 8.8 g. (0.05 mole) of 1,10-diamino-4,7-dioxadecane, 0.5 g. of p-toluenesulfonic acid catalyst, and 300 ml. of p-xylene were heated to reflux with vigorous stirring. The condenser was equipped with a Dean-Stark trap to azeotrope off any water formed in the reaction. After 8 hours of refluxing, 1.6 ml. of water (theory 1.8 ml.) had been collected in the trap. The excess p-xylene was removed by vacuum distillation and the viscous residue dissolved in 100 ml. of N,N-dimethylformamide. The product was precipitated as a sticky semi-solid by the addition of ether while chilling in a Dry Ice-acetone bath. The solvent was decanted and the semi-solid dissolved in methanol. Upon the slow addition of ether, the semi-solid was again precipitated. When this residue was dissolved in ethanol, and acetone slowly added with chilling, a cream-colored solid was obtained which melted at 122–125° C. (softens at 110° C.) when placed on the hot stage at 100° C. Further recrystallizations from the same solvents gave 6.6 g. (42%) of product of the same melting point. The solid melted instantly on the hot stage at 110–115° C. when placed on the hot stage at 110° C. or above.

Analysis.—Calcd. for $(C_{14}H_{26}O_4N_2S)_n$: C, 52.7; H, 8.2; N, 8.8; S, 10.1. Found: C, 51.2; H, 7.6; N, 8.1; S, 8.4.

A molecular weight determination from alcohol was found to be approximately 2079.

EXAMPLE 4

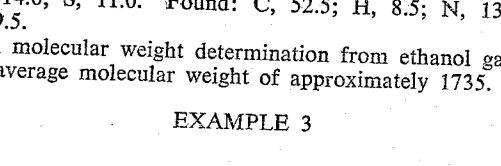
Poly(5,16-Diaza-9,12-Dioxa-4,17-Dioxononadecane-1-Methylsulfonium-p-Toluenesulfonate)

Poly(5,16-diaza-9,12-dioxa - 4,17-dioxo-1-thianonadecane), 3.2 g. (0.01 mole) and 2.7 g. (0.0145 mole) of methyl-p-toluenesulfonate were heated to reflux in 25 ml. of absolute ethanol for 3 hours. The ethanolic solution was concentrated to about a 10 ml. volume, and the solution chilled while slowly adding ether. An oil precipitated, the solvent was decanted, and the process again repeated. After several reprecipitations, the product (3.7 g., 74%) was isolated as an orange, water-soluble oil.

Analysis.—Calcd. for $C_{22}H_{36}N_2O_7S_2$: C, 52.4; H, 7.2; N, 5.6; S, 12.7. Found: C, 51.9; H, 7.3; N, 5.7; S, 12.6.

EXAMPLE 5

Poly(5,16-Diaza-9,12-Dioxa-4,17-Dioxo-1-Thianonadecane)



A mixture of 17.6 g. (0.10 mole) of 1,10-diamino-4,7-dioxadecane, 21.2 g. of β-mercaptopropionic acid (0.20 mole), 0.5 g. of p-toluenesulfonic acid, and 250 ml. of xylene was refluxed with vigorous stirring. The theoretical amount of water collected in a Dean-Stark trap was azeotroped from the reaction mixture after 11 hours. Most of the p-xylene was removed and the gelatinous syrup was dissolved with difficulty in a large volume of hot alcohol. After chilling the solution, 30 g. (85.3%) of a semi-crystalline solid, M.P. 137.5–139.5° C., precipitated from solution.

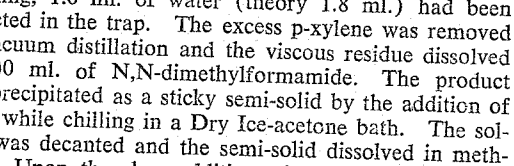
The analytical sample was obtained by recrystallization from a methanol-ether solution, M.P. 139–140.5° C.

Analysis.—Calcd. for $(C_{14}H_{26}N_2O_4S)_n$: C, 52.8; H, 8.1; N, 8.8; S, 9.9. Found: C, 52.8; H, 8.1; N, 8.7; S, 10.1.

The molecular weight of this compound was high, about 5,000–10,000.

EXAMPLE 6

Poly(5,13-Diaza-4,14-Dioxo-9-Oxa-1-Thiahexadecane)



A mixture of 13.2 g. (0.10 mole) of 3,3'-oxydipropylamine, 21.2 g. (0.20 mole) of β-mercaptopropionic acid, 1.0 g. of p-toluenesulfonic acid, and 400 ml. of p-xylene was refluxed with vigorous stirring. The theoretical amount of water, collected in a Dean-Stark trap, was azeotroped from the reaction mixture after 9 hours. The excess p-xylene was removed and ether added, giving a crude white solid of M.P. 135–145° C. The solid was dissolved in 300 ml. of hot N,N-dimethylformamide, filtered through a hot Büchner funnel, and precipitated by the addition of acetone. A white semi-crystalline solid weighing 23.7 g. (86.7%) and melting at 147–150° C. was obtained.

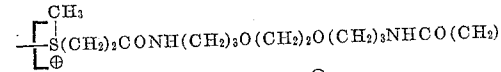
The analytical sample was recrystallized from N,N-dimethylformamide and acetone with M.P. 146.5–149.5° C.

Analysis.—Calcd for $(C_{12}H_{22}N_2O_3S)_n$: C, 52.6; H,

8.0; N, 10.2; S, 11.7. Found: C, 52.5; H, 8.3; N, 9.7; S, 11.6.

EXAMPLE 7

Poly (5,16-Diaza-9,12-Dioxa-4,17-Dioxononadecane-1-Methylsulfonium p-Toluenesulfonate)

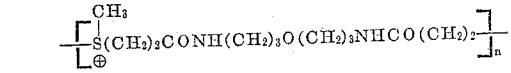


$C_7H_7SO_3^{\ominus}$

This ternarized polymer was prepared in the same manner as the product of Example 4 by heating the polyamide of Example 5 with about a 50% molar excess of methyl-p-toluenesulfonate.

EXAMPLE 8

Poly(5,13-Diaza-4,14-Dioxo-9-Oxahexadecane-1-Methylsulfonium p-Toluenesulfonate)



$C_7H_7SO_3^{\ominus}$

This ternarized polymer was prepared in the same manner as the product of Example 4 by heating together a portion of the product of Example 6 with about a 50 molar percent excess of methyl-p-toluenesulfonate.

EXAMPLE 9

Poly(5,16-Diaza-4,17-Dioxo-1-Thianonadecane)

$$\text{+S(CH}_2\text{)}_2\text{CONH(CH}_2\text{)}_{10}\text{NHCO(CH}_2\text{)}_2\text{+}_n$$

This linear polyamide was prepared according to the method described in Example 2 above by replacing the amine compound used in that example by a molecularly equivalent amount of 1,10-diaminodecane.

EXAMPLE 10

Poly(5,11-Diaza-4,12-Dioxo-1,8-Dithiatetradecane)

$$\text{+S(CH}_2\text{)}_2\text{CONH(CH}_2\text{)}_2\text{S(CH}_2\text{)}_2\text{NHCO(CH}_2\text{)}_2\text{+}_n$$

This polyamide was prepared in the same manner as the polyamide of Example 2 by replacing the amine compound of that example by a molecularly equivalent amount of 1,5-diamine-3-thiapentane.

EXAMPLE 11

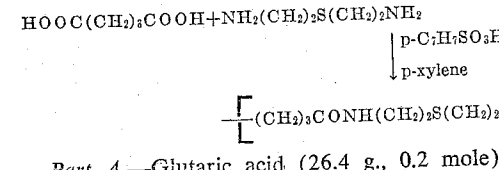
Poly(5,12-Diaza-4,13-Dioxo-1-Thiapentadecane)

$$\text{+S(CH}_2\text{)}_2\text{CONH(CH}_2\text{)}_6\text{NHCO(CH}_2\text{)}_2\text{+}$$

This linear polyamide was obtained according to the method of Example 2 above by replacing the amine of that example by a molecularly equivalent amount of 1,6-diaminohexane.

EXAMPLE 12

Poly(5,11-Diaza-4,12-Dioxo-8-Thiadodecane)



Part A.—Glutaric acid (26.4 g., 0.2 mole), 12.0 g. (0.1 mole) of 3-thia-1,5-diaminopentane, and 0.5 g. of p-toluenesulfonic acid were heated to reflux in 400 ml. of p-xylene. The mixture was vigorously stirred while refluxing with a Dean-Stark trap attached to a condenser. After 6 hours, the theoretical amount of water had been collected in the trap.

The dark oil in the bottom of the flask was stirred vigorously while concentrating the p-xylene mixture to about 50 ml. The product was cooled, ether added, and the solvent decanted. The viscous syrup was dissolved in ethanol, treated with Norite decolorizing carbon, and filtered through a Hyflo bed (silica filter aid). The

orange solution precipitated a solid upon cooling. The solid was filtered by suction. It weighed 10 g., M.P. 105–120° C.

The solid was heated in refluxing alcohol and the undissolved fraction collected. This solid had a melting point of 140–160° C., and after recrystallization from dimethylformamide and ether, melted at 160–164° C. (softens at 150° C.). The solid weighed 2.5 g. A molecular weight determination on the product indicated that this fraction was a polymer (M.W. >3000).

Analysis.—Calc. for $(C_9H_{16}O_2N_2S)_n$: C, 50.0; H, 7.4; N, 13.0; S, 14.8. Found: C, 48.7; H, 6.8; N, 11.3; S, 13.1, 12.9.

The alcoholic extracts from the above separation on dilution with ether precipitated 5.5 g. solid, M.P. 103–106° C. A molecular weight determination on this alcohol-soluble fraction gave 765.

Analysis.—Calc. for $(C_9H_{16}N_2O_2S)_n$: C, 50.0; H, 7.4; N, 13.0; S, 14.8; M. W.—. Found: C, 50.0; H, 7.4; N, 10.9; S, 12.5; M. W., 765.

Infrared analysis on both fractions gave similar curves. They showed —NHCO— bands. The carbonyl band is stronger in the lower molecular weight fraction, suggesting the possibility of acid end groups in this molecule.

The alcohol-insoluble fraction of M.P. 160–164° C., when tested in certain photographic emulsions showed sensitizing properties. The lower molecular weight fraction showed sensitizing activity, but to a lesser degree.

Part B.—In this polymerization reaction, a one-to-one ratio of bisacid to bisamine was used instead of a two-to-one ratio, as in Part A. Glutaric acid, 10.0 g. (0.076 mole), 9.1 g. (0.76 mole) of 3-thia-1,5-diaminopentane, and 0.5 g. of p-toluenesulfonic acid were heated to reflux in 300 ml. of p-xylene. After four hours of refluxing, one milliliter of water had collected in the Dean-Stark trap. The product formed a hard lump in the bottom of the flask, which made stirring difficult. The excess p-xylene was removed and the solid triturated with ether. A pale yellow solid of M.P. 198–200° C. and weighing 16.0 g. was obtained.

The solid was dissolved in hot dimethylformamide, filtered through a hot Buchner funnel, and allowed to crystallize. The gelatinous solid was washed several times with ether. The product turned to a cream colored solid, 13.6 g., M.P. 200–202° C., and proved to be a polymer.

Calculated: C, 50.0; H, 7.4; N, 13.0; S, 14.8. Found: C, 49.1; H, 7.3; N, 13.1, S, 14.3.

The linear polyamide compounds of my invention containing thioether atoms can be effectively employed in photographic silver halide emulsions to increase the sensitivity thereof. These polyamides are non-vulcanizable compounds and are substantially free of disulfide linkages of the type commonly found in vulcanized, rubbery materials. It is known that certain sulfur polymers can be added to photographic silver halide emulsions, although the reason for adding these particular polymeric materials has been for purposes other than increasing the sensitivity of the emulsions. For example, Mueller U.S. Patent 2,699,391, issued January 11, 1955, discloses the addition of polypeptides of α-amino acids to photographic silver halide emulsions as anti-sensitizers or restrainers. Among the amino acids disclosed are those containing disulfide linkages. Such anti-sensitizing polymers are not contemplated by the present invention.

The preparation of photographic silver halide emulsions involves three separate operations: (1) emulsification and digestion of silver halide, (2) the freeing of the emulsion of excess water-soluble salts, usually by washing with water, and (3) the second digestion or "after-ripening" to obtain increased emulsion speed or sensitivity. (Mees, "The theory of the Photographic Process," 1954.) The sensitizers of my invention can be added to the emulsion before the final digestion or after-ripening, or they can be added immediately prior to the coating. My new

photographic sensitizers are unique in that no special final digestion or after-ripening are required in order to obtain optimum sensitization.

The particular quantity of polyamide used in a given emulsion can vary, depending upon the effects desired, degree of ripening, silver content of the emulsion, etc. The amount used is also dependent upon the particular stage at which the sensitizer is added during the preparation of the emulsion. I have found that generally from about 50 mg. to about 3 g. of polyamide per mole of silver halide are quite adequate to accomplish the desired sensitization.

The linear polyamides of my invention can be added to photographic emulsions using any of the well-known techniques in emulsion making. For example, the polyamides can be dissolved in a suitable solvent and added to the silver halide emulsions, or they can be added to the emulsion in the form of a dispersion similar to the technique used to incorporate certain types of color-forming compounds (couplers) in a photographic emulsion. Techniques of this type are described in Jelley et al. U.S. Patent 2,322,027, issued June 15, 1943, and Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957. As indicated above, the solvent should be selected so that it has no harmful effect upon the emulsions, and generally solvents or diluents which are miscible with water are to be preferred. Water alone is a dispersing medium for a few of the polyamides of my invention. In other cases, the polyamide can be dissolved in solvents, such as ethanol, acetone, pyridine, N,N-dimethylformamide, etc., and added to the emulsion in this form. If desired, certain of the polyamides can be prepared in finely-divided form by dispersion in water alone, or in the presence of a suitable dispersing agent and added to the emulsion in this form. It is quite apparent that the polyamides of my invention should have sufficient water-dispersibility so that they can be adsorbed to or associated with the grains of the silver halide present in the emulsion in sufficient amount to sensitize the emulsion. It is apparent that the optimum amount for each of the polyamides will vary somewhat from emulsion to emulsion and from polyamide to polyamide. The optimum amount for any given polyamide can be determined for any particular emulsion by running a series of tests in which the quantity of polyamide is varied over a given range. Exposure of the treated emulsion in conventional photographic testing apparatus, such as an intensity scale sensitometer, will reveal the most advantageous concentrations for that polyamide in that particular emulsion. Such matters are well understood by those skilled in the art.

The emulsions of my invention can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U.S. Patent 1,574,944, issued March 2, 1926, and Sheppard et al. 1,623,499, issued April 5, 1927, and Sheppard and Brigham U.S. Patent 2,410,689, issued November 5, 1946.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum. Representative compounds are ammonium choloropalladate, potassium chloroplatinate, and sodium chloropalladite, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, issued August 31, 1948, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245, issued August 28, 1951, and 2,566,263, issued August 28, 1951.

The emulsions can also be chemically sensitized with gold salts as described in Waller et al. U.S. Patent 2,399,083, issued April 23, 1946, or stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856, issued May 27, 1952, and Yutzy and Leermakers U.S. Patent 2,597,915, issued May 27, 1952. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850, issued November 15, 1949), polyamines, such as diethylene triamine (Lowe and Jones P.S. Patent 2,518,698, issued August 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925, issued September 12, 1950), or bis(β-aminoethyl)sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926, issued September 12, 1950).

The emulsions can also be optically sensitized with cyanine and merocyanine dyes as indicated above, such as indicated above, such as those described in Brooker U.S. Patents 1,846,301, issued February 23, 1932; 1,846,302, issued February 23, 1932; and 1,942,854, issued January 9, 1934; White U.S. Patent 1,990,507, issued February 12, 1935; 2,165,338, issued July 11, 1939; 2,493,747, issued January 10, 1950; and 2,739,964, issued March 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued January 10, 1950; Sprague U.S. Patents 2,503,776, issued April 11, 1950, and 2,519,001, issued August 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued January 19, 1954; Heseltine U.S. Patent 2,734,900, issued February 14, 1956; Van Lare U.S. Patent 2,739,149, issued March 20, 1956; and Kodak Limited British Patent 450,958, accepted July 15, 1936.

The emulsions can also be stabilized with the mercury compounds of Allen, Byers and Murray U.S. Patent 2,728,663, issued December 27, 1955; Carroll and Murray U.S. Patent 2,728,664, issued December 27, 1955; and Leubner and Murray U.S. Patent 2,728,665, issued December 27, 1955; the triazoles of Heimbach and Kelly U.S. Patent 2,444,608, issued July 6, 1948; the azaindenes of Heimbach and Kelly U.S. Patents 2,444,605 and 2,444,606, issued July 6, 1948; Heimbach U.S. Patents 2,444,607, issued July 6, 1948, and 2,450,397, issued September 28, 1948; Heimbach and Clark U. S. Patent 2,444,609, issued July 6, 1948; Allen and Reynolds U.S. Patents 2,713,541, issued July 19, 1955, and 2,743,181, issued April 24, 1956; Carroll and Beach U.S. Patent 2,716,062, issued August 23, 1955; Allen and Beilfuss U.S. Patent 2,735,769, issued February 21, 1956; Reynolds and Sagal U.S. Patent 2,756,147, issued July 24, 1956; Allen and Sagura U.S. Patent 2,772,164, issued November 27, 1956, and those disclosed by Birr in "Z. wiss. Phot.," vol. 47, 1952, pages 2–28; the disulfides of Kodak Belgian Patent 569,317, issued July 31, 1958; the triazaindenes of Allen and Sagura U.S. Patent 2,772,164, issued November 27, 1956, etc.; the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038, issued September 27, 1938, or Allen and Wilson U.S. Patent 2,694,716, issued November 16, 1954 (e.g., decamethylene-bis-benzothiazolium perchlorate); the zinc and cadmium salts of Jones U.S. patent application Serial No. 493,047, filed March 8, 1955 (now U.S. Patent 2,839,405, issued June 17, 1958) etc.

The emulsions may also contain speed-increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623, issued February 3, 1942; Carroll and Allen U.S. Patent 2,288,226, issued June 30, 1942; and Carroll and Spence U.S. Patent 2,334,864, issued November 23, 1943; and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162, issued May 10, 1955.

The emulsions may contain a suitable gelatin plasticizer such as glycerin; a dihydroxy alkane such as 1,5-pentane diol as described in Milton and Murray U.S. application Serial No. 588,951, filed June 4, 1956 (now U.S. Patent 2,960,404, issued November 15, 1960); an ester of an ethylene bis-glycolic acid such as ethylene bis(methyl glycolate) as described in Milton U.S. application Serial No. 662,564, filed May 31, 1957 (now U.S. Patent 2,904,434, issued September 15, 1959); bis-(ethoxy

diethylene glycol) succinate as described in Gray U.S. application Serial No. 604,333, filed August 16, 1956 (now U.S. Patent 2,940,854, issued June 14, 1960), or a polymeric hydrosol as results from the emulsion polymerization of a mixture of an amide of an acid of the acrylic acid series, an acrylic acid ester and a styrene-type compound as described in Tong U.S. patent application Serial No. 311,319, filed September 24, 1952 (now U.S. Patent 2,852,386, issued September 16, 1958). The plasticizer may be added to the emulsion before or after the addition of a sensitizing dye, if used.

The emulsion may be hardened with any suitable hardener for gelatin such as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in White U.S. Patent 2,080,019, issued May 11, 1937; a compound having a plurality of acid anhydride groups such as 7,8-diphenylbicyclo(2,2,2)-7-octene-2,3,5,6-tetracarboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloyl chloride or naphthalene-1,5-disulfonyl chloride as described in Allen and Carroll U.S. Patents 2,725,294 and 2,725,295, both issued November 29, 1955; a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in Allen and Byers U.S. Patent 2,725,305, issued November 29, 1955; a biester of methane-sulfonic acid such as 1,2-di-(methanesulfonoxy)-ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued December 6, 1955; 1,3-dihydroxymethylbenzimidazol-2-one as described in July, Knott and Pollak U.S. Patent 2,732,316, issued January 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2–3 carbon atoms, such as β-methyl glutaraldehyde bis-sodium bisulfite as described in Allen and Burness Canadian Patent 588,451, issued December 8, 1959; a bis-aziridine carboxamide such as trimethylene bis(1-aziridine carboxamide) as described in Allen and Webster U.S. patent application Serial No. 599,891, filed July 25, 1956 (now U.S. Patent 2,950,197, issued August 23, 1960); or 2,3-dihydroxy dioxane as described in Jeffreys U.S. patent application Serial No. 624,968, filed November 29, 1956 (now U.S. Patent 2,870,013, issued January 20, 1959).

The emulsions may contain a coating aid such as saponin; a lauryl or oleoyl monoether of polyethylene glycol as described in Knox and Davis U.S. Patent 2,831,766, issued April 22, 1958; a salt of a sulfated and alkylated polyethylene glycol ether as described in Knox and Davis U.S. Patent No. 2,719,087, issued September 27, 1955; an acylated alkyl taurine such as the sodium salt of N-oleoyl-N-methyl taurine as described in Knox, Twardokus and Davis U.S. Patent 2,739,891, issued March 27, 1956; the reaction product of a dianhydride of tetracarboxybutane with an alcohol or an aliphatic amine containing from 8 to 18 carbon atoms which is treated with a base, for example, the sodium salt of the monoester of tetracarboxybutane as described in Knox, Stenberg and Wilson U.S. patent application Serial No. 485,812, filed February 2, 1955 (now U.S. Patent 2,843,487, issued July 15, 1958); a water-soluble maleopimarate or a mixture of a water-soluble maleopimarate and a substituted glutamarate salt as described in Knox and Fowler U.S. Patent 2,823,123, issued February 11, 1958; an alkali metal salt of a substituted amino acid such as disodium N-(carbo-p-tert. octylphenoxypentaethoxy)-glutamate as described in Knox and Wilson U.S. patent application Serial No. 600,679, filed July 30, 1956; or a sulfosuccinamate such as tetrasodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate or N-lauryl disodium sulfosuccinamate as described in Knox and Stenberg U.S. patent application Serial No. 691,125, filed October 21, 1957.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there may be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound. Some colloids which may be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19–26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued August 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide having a combined acrylamide content of 30–60% and a specific viscosity of 0.25–1.5 on an imidized polyacrylamide of like acrylimide content and viscosity as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued October 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued October 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in U.S. application Serial No. 527,872 of Illingsworth, Dann and Gates, filed August 11, 1954 (now U.S. Patent 2,852,382, issued September 16, 1958).

If desired, compatible mixtures of two or more of these colloids may be employed for dispersing the silver halide in its preparation. Combinations of these antifoggants, sensitizers, hardeners, etc., may be used.

The addenda which I have described may be used in various kinds of photographic emulsions. In addition to being useful in X-ray and other nonoptically sensitized emulsions, they may also be used in orthochromatic, panchromatic, and infrared sensitive emulsions. They may be added to the emulsion before or after any sensitizing dyes which are used. Various silver salts may be used as the sensitive salt, such as silver bromide, silver iodide, silver chloride, or mixed silver halides, such as silver chlorobromide or silver bromoiodide. The agents may be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-packet type, such as described in Godowsky U.S. Patent 2,698,794, issued January 4, 1955, or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243, issued April 8, 1952. These agents can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent images predominantly inside the silver halide crystal, such as those described in Davey and Knott U.S. Patent 2,592,250, issued April 8, 1952.

They may also be used in emulsions intended for use in diffusion transfer processes which utilize the undeveloped silver halide in the nonimage areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott U.S. Patent 2,352,014, issued June 20, 1944, and Land U.S. Patents 2,584,029, issued January 29, 1952; 2,698,236, issued December 28, 1954, and 2,543,181, issued February 27, 1951; and Yackel et al. U.S. patent application Serial No. 586,705, filed May 23, 1956. They may also be used in color transfer processes which utilize the diffusion transfer of an image-wise distribution of developer, coupler or dye, from a light-sensitive layer to a second layer, while the two layers are in close proximity to one another. Color processes of this type are described in Land U.S. Patents 2,559,643, issued July 10, 1951, and 2,698,798, issued January 4, 1955; Land and Rogers Belgian Pat-

ents 554,933 and 554,934, granted August 12, 1957; International Polaroid Belgian Patents 554,212, granted July 16, 1957, and 554,935, granted August 12, 1957; Yutzy U.S. Patent 2,756,142, issued July 24, 1956, and Whitmore and Mader U.S. patent application Serial No. 734,141, filed May 9, 1958.

The following examples will serve to illustrate more fully the manner of sensitizing photographic silver halide emulsions according to my invention.

In ordinary photographic silver bromoiodide emulsion containing a sensitizing dye, a sulfur sensitizer of the type mentioned in Sheppard U.S. Patent 1,623,499, mentioned above, and gold sensitized in the manner indicated in U.S. Patent 2,399,083, mentioned above, was divided into several portions. Linear polyamide compounds of the type obtained in the above examples were then added in solutions in an organic solvent, such as ethanol or N,N-dimethylformamide, in the amounts indicated in the table. The various portions of emulsions were then coated on a transparent support, such as cellulose acetate and dried. The dried coatings were exposed for about 1/25 sec. to daylight quality radiation in an Eastman Ib Sensitometer. The exposed coatings were then developed for abut 5 minutes in a photographic developer having the following composition:

	Grams
N-methyl-n-aminophenol sulfate	2.5
Hydroquinone	2.5
Sodium sulfite (dry)	30.0
Sodium borate	10.0
Potassium bromide	0.5
Water to make one liter.	

The relative speed (as compared with a portion of the emulsion containing no polyamide), gamma and fog for each of the coatings were then measured. The results are given in the following table:

TABLE I

Coating No.	Polymer of Example (g./mol. AgX)	Sensitometric Data		
		Speed	Gamma	Fog
1(a)	none (control)	100	1.23	.13
(b)	1 (0.9)	129	1.13	.16
2(c)	none (control)	100	1.16	.13
(d)	2 (0.03)	132	1.39	.20
(e)	2 (3.0)	195	1.05	.45
3(f)	3 (0.3)	224	.98	.25
4(g)	4 (0.3)	200	1.02	.24
5(h)	none (control)	100	1.20	.13
(i)	5 (0.09)	220	1.05	.21
6(j)	none (control)	100	1.37	.14
(k)	6 (.03)	166	1.30	.14
(l)	6 (0.3)	269	.97	.24
7(m)	none (control)	100	1.20	.13
(n)	7 (0.3)	214	.97	.21
(o)	7 (0.9)	240	1.04	.27
8(p)	none (control)	100	1.36	.16
(q)	8 (0.3)	195	1.05	.39
9(r)	none (control)	100	1.37	.14
(s)	9 (3.0)	126	1.20	.12

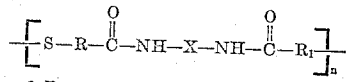
The effect of my new polyamides has been illustrated above with particular reference to ordinary photographic silverbromiodide emulsions, although it is to be understood that other silver halide emulsions can be employed to like advantage. The polyamides of my invention can be used in emulsions which are acidic in character or in emulsions which are alkaline. Of course, when adding polyamides to such emulsions, it is generally desirable to adjust the pH of the sensitizing solution so that it will not seriously alter the pH of the emulsion to be treated. It is apparent that certain of the polyamides may be present in salt form when present in acidic (e.g., where polyamide contains amino groups) or alkaline (e.g., where polyamide contains free acid groups) emulsions, and it is to be understood that my invention contemplates these polyamides either in their salt or non-salt forms.

Among the most effective polyamides of my invention are those obtained from the diamines of Formula III above, wherein the alkylene linkage (X) is interrupted by one or more polar groups, such as oxygen, sulfur, amino, etc. Where the alkylene chain is interrupted by non-polar linkages, such as phenylene, and the like, useful results can sometimes be obtained. Of course, some of the polyamides of my invention can contain acidic groups on the terminal linkages, and it is to be understood that my invention contemplates using these polyamides in the form of their non-neutralized solutions, as well as in solutions which have been neutralized with alkali or ammonia. The amount of ester used to increase the solubility of my new polyamides can be varied. For example, I have found that from about 10 to 90% of the sulfur atoms in the linear chains of my polymers can be ternarized by heating with esters, such as methyl, p-toluenesulfonate, ethyl sulfate, methyl sulfate, etc., to effectively increase the solubility of the polymers without affecting their photographic properties to a prohibitive degree, as illustrated above.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

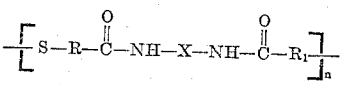
What I claim as my invention and desire secured by Letters Patent of the United States is:

1. A photographic silver halide emulsion sensitized with a linear polyamide consisting essentially of polymer units represented by the following general formula:



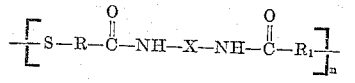
wherein R and R_1 each represents an alkylene group, X represents a divalent aliphatic radical and *n* represents a positive integer of at least 2, said polymer having a molecular weight of at least about 350.

2. A photographic silver halide emulsion containing a sensitizing amount of (1) a labile sulfur compound (2) a gold sensitizer and (3) a linear polyamide consisting essentially of polymer units represented by the following general formula:

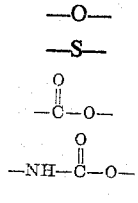


wherein R and R_1 each represents an alkylene group, X represents a divalent aliphatic radical and *n* represents a positive integer of at least 2, said polymer having a molecular weight of at least about 350.

3. A photographic silver halide emulsion containing a sensitizing amount of a linear polyamide consisting essentially of polymer units represented by the following general formula:



wherein R and R_1 each represents a hydrocarbon alkylene group containing from 1 to 4 carbon atoms, X represents a member selected from the class consisting of a hydrocarbon alkylene group containing from 2 to 10 carbon atoms and an alkylene group wherein the chain of carbon atoms is interrupted by a radical selected from the class consisting of

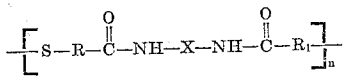


and

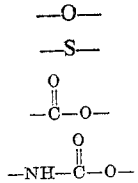


wherein R_2 represents a member selected from the group consisting of a hydrogen atom and an alkyl group containing from 1 to 3 carbon atoms, and *n* represents a positive integer of at least about 2, said polymer having a molecular weight of at least about 350.

4. A photographic silver halide emulsion containing a sensitizing amount of (1) a labile sulfur compound, (2) a gold sensitizer and (3) a linear polyamide consisting essentially of polymer units represented by the following general formula:



wherein R and R_1 each represents a hydrocarbon alkylene group containing from 1 to 4 carbon atoms, X represents a member selected from the class consisting of a hydrocarbon alkylene group containing from 2 to 10 carbon atoms and an alkylene group wherein the chain of carbon atoms is interrupted by a radical selected from the class consisting of

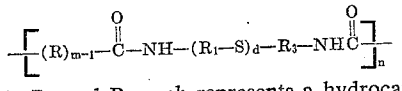


and



wherein R_2 represents a member selected from the group consisting of a hydrogen atom and an alkyl group containing from 1 to 3 carbon atoms, and *n* represents a positive integer of at least about 2, said polymer having a molecular weight of at least about 350.

5. A photographic silver halide emulsion containing a sensitizing amount of a linear polyamide consisting essentially of polymer units represented by the following general formula:



wherein R, R_1 and R_3 each represents a hydrocarbon alkylene group, *d* represents a positive integer of from 1 to 3, *m* represents a positive integer of from 1 to 2 and *n*

represents a positive integer of at least about 2, said polymer having a molecular weight of at least about 350.

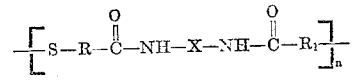
6. A photographic silver halide emulsion containing a sensitizing amount of poly(5,16-diaza-9,12-dioxa-4,17-dioxo-1-thianonadecane, said polymer having a molecular weight of at least about 350.

7. A photographic silver halide emulsion containing a sensitizing amount of poly(4,14-dioxo-9-methyl-1-thia-5,9,13-triazahexadecane), said polymer having a molecular weight of at least about 350.

8. A photographic silver halide emulsion containing a sensitizing amount of poly(5,13-diaza-4,14-dioxo-9-oxa-1-thiahexadecane), said polymer having a molecular weight of at least about 350.

9. A photographic silver halide emulsion containing a sensitizing amount of poly(5,16-diaza-9,12-dioxa-4,17-dioxononadecane-1-methylsulfonium p-toluenesulfonate, said polymer having a molecular weight of at least about 350.

10. A photographic silver halide emulsion sensitized with a ternary salt of a linear polyamide consisting essentially of polymer units represented by the following general formula:



wherein R and R_1 each represents an alkylene group, X represents a divalent aliphatic radical and *n* represents a positive integer of at least 2, said polymer having a molecular weight of at least about 350.

11. A photographic silver halide emulsion containing a sensitizing amount of poly(5,13-diaza-4,14-dioxo-9-oxahexadecane-1-methylsulfonium p-toluenesulfonate, said polymer having a molecular weight of at least about 350.

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