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3,017,271

PHOTOGRAPHIC EMULSIONS SENSITIZED WITH ALKYLENE OXIDE POLYMERS AND QUATERNARY AMMONIUM SALTS

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14 Claims. (Cl. 96-107)

This application relates to photography and particularly to sensitizing photographic emulsions.

This application is a division of my copending U.S. patent application Serial No. 550,495, filed December 1, 1959, now U.S. Patent 2,886,437, granted May 12, 1959, for Photographic Emulsions Sensitized with Alkylene Oxide Polymers and Quaternary Ammonium Compounds.

It is well known that silver halide emulsions may be chemically sensitized with a variety of materials in order to increase the speed and generally the gamma of the emulsion, as opposed to optical sensitization in which the optical range of sensitivity is increased. Chemical sensitization usually results either from the formation of silver sulfide on the surface of the silver halide crystal, thus increasing sensitivity, or from the formation of small amounts of silver from the reduction of silver halide. Other classes of compounds, such as certain ethylene oxide condensation products and certain cationic surface-active salts increase sensitivity of silver halides without apparently entering into chemical combination with the silver halide.

Carroll U.S. patent 2,271,623, Carroll and Allen U.S. patent 2,288,226 and Carroll and Spence U.S. patent 2,334,864 describe the chemical sensitization of silver halide emulsions with quaternary ammonium compounds.

I have now found that the light-sensitivity of silver halide emulsions which have been sensitized with alkylene oxide polymers not containing a quaternary ammonium group, with and without optical sensitizing dyes, may be further increased by the use of quaternary ammonium compounds, and that this increase in sensitivity is not accompanied by an increase in graininess. The polyalkylene oxide polymers and quaternary ammonium compounds can be used in combination in several ways to produce sensitivity increases, i.e., the compounds may be added to the emulsion, the emulsion may be treated with the compounds before exposure and development, or by the addition of at least one of the compounds to the developer. Thus it is possible to produce the sensitivity increases by using one of the above procedures for both compounds (e.g., adding both to the emulsion before coating) or by using the compounds in different procedures (e.g., adding the polyethylene oxide to the emulsion and the quaternary ammonium salt to the developer), as illustrated by the examples hereinafter.

The quaternary ammonium silver halide sensitizing agents useful in the invention in conjunction with the alkylene oxide polymers include a wide variety of well known quaternary ammonium salts such as disclosed in U.S. Patents 2,288,226 and 2,271,623.

An important group of these salts are the tetraalkyl quaternary ammonium salts having the general formula

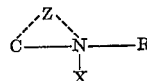


in which X is an anion or acid radical, for example, halide, p-toluene sulfonate, alkyl sulfate or perchlorate, R, R₁, R₂ and R₃ are alkyl groups of which at least one has a

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chain of seven or more atoms such as carbon atoms, carbon atoms plus oxygen atoms, sulfur atoms or nitrogen atoms and ring systems, while the remaining R groups are alkyl such as methyl, ethyl, butyl, and benzyl as exemplified hereinafter.

Another group of the quaternary ammonium salts, in which the quaternary nitrogen atom is a part of a ring system, has the general formula



where X is as above and R represents a chain of at least seven atoms such as above; however, R may be an aralkyl group as small as β-phenyl ethyl, and Z represents the atoms necessary to complete a cyclic structure such as a pyridyl, α-picoly, piperidyl or morpholinyl nucleus. If R contains a second quaternary nitrogen atom, a long chain may link the nitrogen atoms as in the bis-quaternary ammonium compounds tabulated hereinafter.

Examples of the quaternary ammonium salt sensitizers are given in the following table, the compound number for each salt being that utilized in the emulsion examples hereinafter.

Compound No.	
Quat. I	Decamethylene - α - ω - bis(oxymethylpyridinium perchlorate)
" II	Laurylpyridinium perchlorate
" III	Decamethylene - bis - (oxymethyl-α-picolinium perchlorate)
" IV	p-Xylylene-bis-(pyridinium perchlorate)
" V	Hexamethylene - bis(oxymethylpyridinium perchlorate)
" VI	Hexadecylpyridinium bromide
" VII	Decamethylene - bis(oxymethyldimethylbenzylammonium perchlorate)
" VIII	Decamethylene - bis(N-methylpiperidinium perchlorate)
" IX	Lauryl pyridinium-p-toluenesulfonate
" X	N - n - Tetradecyl-N-methylmorpholinium-p-toluene sulfonate
" XI	Lauryl trimethylammonium-p-toluene sulfonate
" XII	n - Myristyl-trimethylammonium-p-toluene sulfonate
" XIII	Decamethylene-bis-trimethylammonium bromide
" XIV	Decamethylene-bis-trimethylammonium perchlorate
" XIVa	Tetradecamethylene-bis(pyridinium perchlorate)

These quaternary ammonium compounds can be obtained by the methods described in the above patents.

The quantity of quaternary ammonium compound which is most advantageously employed varies with the nature of the quaternary ammonium compound and with the nature of the emulsion. Ordinarily, the most advantageous concentration has been found to be between about 50 mgs. and 5000 mgs. of the quaternary ammonium compound per gram mole of silver halide in the emulsion, although greater or smaller concentrations can be employed. We have found that excesses of the quaternary ammonium compound are to be avoided since excesses produce fog in the emulsions. The optimum range of concentration for any quaternary ammonium compound described herein is ordinarily fairly narrow and can best be determined by employing a series of concentrations of the quaternary ammonium compound separately in several batches of the same emulsion and determining the

sensitivity of the several batches before and after incorporation of the quaternary ammonium compound, in the usual manner which is, of course, well known to those skilled in the art.

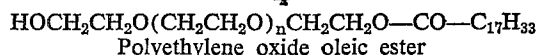
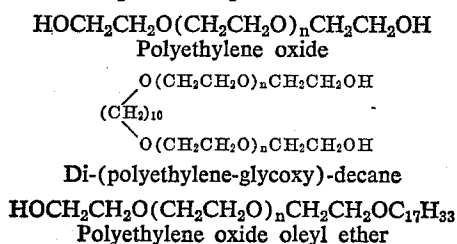
The alkylene oxide polymers used to sensitize the emulsions may be of various types. The alkylene oxides from which the polymers are derived contain from 2 to 4 carbon atoms, e.g., ethylene oxide, propylene oxide and butylene oxide. The preparation of polymers from these compounds is described in Ellis, *The Chemistry of Synthetic Resins* (1935), pages 990 to 994. These compounds are also referred to as polyalkylene glycols and their use as sensitizers for silver halide emulsions is described in U.S. Patents 2,423,549 and 2,441,389. The alkylene oxide derivatives may be prepared by condensing an organic compound containing an active hydrogen atom with an alkylene oxide polymer, or by condensing the active hydrogen compound with the alkylene oxide during the polymerization of the latter material.

Various derivatives of alkylene oxides may also be used to sensitize the emulsions, e.g., condensation products of alkylene oxide with organic compounds containing an active hydrogen atom. Examples of "active hydrogen organic compounds," i.e., compounds in which a hydrogen atom may be replaced by reaction of the compound with metallic sodium, methylmagnesium iodide, etc., include alcohols, amines, mercaptans, acids, amides, hydrocarbons such as acetylene, and compounds having the active hydrogen in a methylene group such as dibenzoylmethane. More specifically, we may employ condensation products of alkylene oxide with glycols such as those having from 8 to 18 carbon atoms as described in U.S. Patent 2,240,472 and British Patent 443,559 as well as condensation products of alkylene oxides with aliphatic alcohols, condensation products of alkylene oxides with aliphatic acids, e.g., lauric acid and glycine, condensation products of alkylene oxides with aliphatic amines or amides, e.g., glycine and lauryl amide, and condensation products of alkylene oxides with phenols, e.g., phenol. The preparation of these condensation products is described in U.S. Patent 1,970,578. Condensation products of alkylene oxides with hexitol ring dehydration products as described in U.S. Patent 2,400,532 may also be employed.

In each case the polyalkylene oxide or derivative of alkylene oxide should have a molecular weight of at least 300. Condensation products of ethylene oxide with long chain alcohols, acids, amines or amides should have a molecular weight of about 700. In general, the best results are obtained with the condensation products of ethylene oxide with long chain compounds having a chain length of 12 or more carbon atoms and with ethylene oxide polymers having a molecular weight of 1500 to 4000 or more.

When employing optically sensitized emulsions the optical sensitizing dyes are advantageously employed in about their optimum concentration which ordinarily lies between about 10 mgs. and 40 mgs. of optical sensitizing dye per liter of emulsion containing about 0.25 gram mole of silver halide although concentrations above or below the optimum concentration can be employed.

The alkylene oxide derivatives used to sensitize the emulsions may be illustrated by the following specific examples, although my invention is in no way limited to the use of these specific compounds.



where n = an integer greater than about 10.

Polyethylene oxide nonyl phenol ether
N-methyl myristylamino polyethylene oxide
N-methyl-n-dodecylamino polyethylene oxide

N-methylmyristylaminopolyethylene oxide 1045 can be prepared as follows:

In a flask equipped for gas addition is placed 10 parts of N-methylmyristylamine (prepared by lithium aluminum hydride reduction of N-methylmyristamide) and a catalytic amount of boron fluoride-ethyl ether complex. Ethylene oxide is added slowly over a period of 12 to 15 hours until 46 parts of the gas is absorbed. The optimum reaction temperature is 100 to 105° C. The product so obtained is a light amber colored waxy material; the color may be removed partially by treatment with charcoal in a suitable solvent.

This material is representative of a number of condensation products of ethylene oxide with secondary amines the alkyl chain of which should contain at least nine carbon atoms and the polyethylene oxide chain should have a molecular weight of at least 500.

The preparation of silver halide emulsions involves three separate operations: (1) the emulsification and digestion or ripening of the silver halide, (2) the freeing of the emulsion from aqueous soluble salts usually by washing, (3) the second digestion or after-ripening to obtain increased sensitivity (Mees, *The Theory of the Photographic Process*, 1942, page 3). The sensitizing agents may be added at any stage, preferably after the final digestion.

The photographic emulsions which we use are of the developing-out type and best results have been obtained with gelatino-silver bromiodide emulsions. However, emulsions of varying halide content may be used.

The emulsions may be chemically sensitized by any of the accepted procedures, in addition to or in combination with the sensitizing with alkylene oxide polymers. The emulsions may be digested with naturally active gelatin, or sulfur compounds may be added such as those described in Sheppard U.S. Patents 1,574,944 and 1,623,499, and Sheppard and Brigham U.S. Patent 2,410,689.

The emulsions may also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium and platinum, all of which belong to group VIII of the periodic table of elements and have an atomic weight greater than 100. Representative compounds are ammonium chloropalladate, potassium chloroplatinate and sodium chloropalladate, 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, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245 and 2,566,263.

The emulsions may also be chemically sensitized with gold salts as described in Waller and Dodd U.S. Patent 2,399,083 or stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856 and Yutzy and Leermakers U.S. Patent 2,597,915. Suitable compounds are potassium chloraurate, potassium aurithiocyanate, potassium chloraurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

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

The emulsions may also be stabilized with the mercury compounds of Allen, Byers and Murray U. S. application Serial No. 319,611, Carroll and Murray U.S. application Serial No. 319,612 and Leubner and Murray U.S. appli-

Other stabilizing agents may be added to the emulsions containing the quaternary ammonium compounds and polyalkylene oxides such as cadmium chloride, cadmium nitrate, cobalt nitrate, manganese chloride, manganese sulfate, zinc chloride, zinc nitrate and zinc sulfate.

These and other azaindene compounds useful for this purpose are disclosed in U.S. Patent 2,716,062, and

Zeitschrift für Wiss. Phot. 47, 2-28 (1952).

The following examples illustrate my invention.

Compound No.

Compound No.		50
PEO XV	Oleyl ether polyethylene oxide 1800	
PEO XVI	Oleic ester polyethylene oxide 1000	
PEO XVII	Oleic ester polyethylene oxide 6000	
PEO XVIII	Nonylphenol ether polyethylene oxide 1145	
PEO XIX	N-Methylmyristylamino polyethylene oxide 1045	55
PEO XX	Oleyl ether polyethylene oxide 1500	
PEO XXI	N-Methyl-n-dodecylamino polyethylene oxide 1145	
PEO XXII	Polyethylene oxide 1540	60
PEO XXIII	Polyethylene oxide 4000	

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Addition of the polyethylene oxide, quaternary ammonium salt and azaindene to the emulsion before coating

To samples of a panchromatic gelatin-silver bromide emulsion which has been digested with a sulfur compound such as disclosed in Sheppard U.S. Patent 1,574,944 and potassium chloroaurate were added the compounds shown in the following table. The emulsions were coated on a cellulose acetate support in the conventional manner. The coatings were exposed on an Eastman type I-b sensitometer and processed for 5 minutes in Kodak Developer DK-50 having the following composition with the results shown in the following table, speed being read as 30/E where E is the exposure in meter candle seconds required to produce a density of 0.2 over fog:

Developer DK-50:	Grams
N-methyl-p-aminophenol sulfate-----	2.5
Hydroquinone-----	2.5
Sodium sulfite, desiccated-----	30.0
Sodium metaborate-----	10.0
Potassium bromide-----	0.5
Water to make 1 liter.	

Sample	Compound	Grams per mole AgX	30/E	Gamma	Fog
788		0	5,700	.91	.03
789	Aza	1.5	7,050	.87	.04
801	{ Aza PEO XV	{ 1.5 5.0	9,900	.97	.04
792	{ Aza Quat I	{ 1.5 7.5	12,200	.96	.09
804	{ Aza PEO XV Quat I	{ 1.5 5.0 2.5	13,400	1.07	.10

This example readily shows the supersensitizing effect of the combination of the polyethylene oxide with the quaternary ammonium compound. Sample 801 containing the oxide has a speed of only 9900, and sample 792 containing the pyridinium compound has a speed of only 12,200, whereas the combination of the two in the emulsion as in sample 804 yields a speed of 13,400.

Addition of the polyethylene oxide and tetraazaindene to the emulsion and the quaternary ammonium salt to the developer

Coatings were prepared as described in Example 1, except the emulsion contained the following addenda and was processed in the following developers for the indicated times:

Sample	Compound	Grams per mole AgX	5' DK-50			5' DK-50+0.5 g./l. Quat XIII		
			30/E	Gamma	Fog	30/E	Gamma	Fog
694-----		0	3,950	1.17	.30	6,400	1.18	.32
695-----	Aza-----	1.0	5,700	1.09	.30	9,900	1.10	.33
696-----	PEO XV----	0.65	7,050	1.13	.30	9,250	1.17	.32
697-----	{PEO XV---- Aza-----}	0.65 1.0	8,650	1.04	.32	11,900	1.19	.32

EXAMPLE 3

Addition of quaternary ammonium salt and tetraazaindene to the emulsion and the polyethylene oxide to the developer

Emulsion is similar to that described in Example 1, containing the following addenda, and exposed and processed as indicated:

Sample	Compound	Grams per mole AgX	3' DK-50			3' DK-50+2.0 g./l. PEO XV		
			30/E	Gamma	Fog	30/E	Gamma	Fog
472	Aza	13.0	7550	1.40	.20	12,200	1.25	.30
474	Aza	13.0	10,600	1.15	.23	14,000	1.18	.32
	Quat I	1.5						

EXAMPLE 5

Addition of one or all of the polyethylene oxide, the quaternary ammonium salt, and the azaindene, either to the emulsion or to the developer

The coatings were prepared as described in Example 1, except that the emulsion contained the addenda described in the following table. The coatings were exposed

on a I-b sensitometer and processed in the developers given, for the indicated times.

Sample	Compound	Grams per mole AgX	5' DK-50		5' DK-50+2 g./l. PEO XV		5' DK-50+1 g./l. Quat I		5' DK-50+2 g./l. PEO XV+1 g./l. Quat I	
			30/E	Fog	30/E	Fog	30/E	Fog	30/E	Fog
907			7,700	.25	10,900	.28	15,800	.42	19,000	.43
908	Aza	1.7	8,850	.25	12,200	.29	16,900	.47	22,000	.48
909	Aza	1.7	15,000	.31	15,000	.33	19,500	.55	21,500	.53
	PEO XV	1.0								
910	Aza	1.7	15,000	.37	16,500	.39	16,500	.53	22,500	.53
	Quat I	2.5								
911	Aza	1.7	20,000	.45	19,000	.46	17,700	.61	23,000	.60
	PEO XV	1.0								
	Quat I	2.5								

EXAMPLE 4

Addition of the polyethylene oxide, quaternary ammonium salt and stabilizing agents to the emulsion before coating

The coatings were prepared as described in Example 1, except that the emulsion contained the addenda described in the following table. The coatings were exposed on a I-b sensitometer and processed in the developer given for the times indicated. For convenience the speeds indicated in the table are measured as 100 (1-log E), where E is the exposure in meter candle seconds required to produce a density of 0.3 above fog.

The data can be quickly assessed by noting that the speed values (of Samples 907, 908 and 909) 7700, 10,900, 8850, 12,200, and 15,000 represent development with the quaternary compound present in neither emulsion nor developer.

The example clearly illustrates that the quaternary ammonium compounds are highly effective when present in the developer alone or together with the polyethylene oxides, for the development of emulsions free of, or containing either or both of these sensitizing agents.

Sample	Compound	Grams per Mole AgX	5' DK-50			12' DK-50		
			Speed	Gamma	Fog	Speed	Gamma	Fog
668	PEO XV	1.5	360	.58	.11	397	.87	.19
	Aza	2.0						
672	PEO XV	1.5	363	.64	.06	394	.99	.14
	Aza	2.0						
	CdCl ₂	20.0						
671	PEO XV	1.5	380	.56	.20	398	.73	.44
	Aza	2.0						
	Quat. XIVa	0.5						
675	PEO XV	1.5	385	.65	.12	407	1.01	.23
	Aza	2.0						
	Quat. XIVa	0.5						
	CdCl ₂	20.0						
676	PEO XV	1.5	363	.63	.05	394	.99	.12
	Aza	2.0						
	EDGS ¹	20.0						
679	PEO XV	1.5	386	.67	.09	407	.98	.20
	Aza	2.0						
	Quat. XIVa	0.5						
	CdCl ₂	20.0						
	EDGS ¹	20.0						

¹ Bis(ethoxy diethyleneglycol)succinate—Gray U.S. patent application Serial No. 532,756, filed September 6, 1955.

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EXAMPLE 6

Addition of one of the polyethylene oxide, the quaternary ammonium salt, or the azaindene either directly to the liquid emulsion, or by means of a pre-exposure bath of the coated film

The coatings were prepared as described in Example 1, except that the emulsion contained the addenda described below. The coatings, after being bathed for 5 minutes in the solutions described, were dried, exposed on a I-b sensitometer, and developed for 5 minutes in Kodak Developer DK-50.

Sample	Compound in Emulsion	Gms./Mole AgX	Compound in Pre-exposure bath	gms./l.	30/E	Fog
3908	Aza	1.7	none	9,500	.31	
3908	Aza	1.7	Quat I.	1.25	17,700	.46
3909	Aza	1.7	none	13,400	.34	
3909	PEO XV	1.0	none			
3909	Aza	1.7	Quat I.	1.25	16,900	.68
3909	PEO XV	1.0				
3911	Aza	1.7	none	15,800	.45	
3911	PEO XV	1.0				
3911	Quat I.	2.5				

EXAMPLE 7

Addition of both the polyethylene oxide and the quaternary ammonium salt to the emulsion before coating

To an emulsion similar to that described in Example 1, the following were added. The coatings were exposed and processed as in Example 1.

Sample	Compound	Grams per mole AgX	30/E	Gamma	Fog
125	Aza	1.7	7,550	1.25	.20
133	PEO XV	0.75	11,400	1.10	.24
133	Aza	1.7			
127	Quat III	0.5	9,900	1.15	.27
127	Aza	1.7			
135	PEO XV	0.75	15,000	1.11	.37
135	Aza	1.7			
135	Quat III	0.5			

EXAMPLE 8

Addition of different polyethylene oxides and quaternary ammonium salts to the emulsion before coating

To an emulsion similar to that described in Example 1 the following were added. The coatings were exposed and processed as in Example 1.

Sample	Compound	Grams per Mole AgX	30/E	Gamma	Fog
3009	PEO XV	0.75	9,700	1.15	.24
3009	Aza	1.7			
3014	PEO XV	0.75	12,800	1.21	.24
3014	Quat IV	0.75			
5344	Aza	1.7	7,900		.20
5345	Aza	1.7	9,700		.24
5345	PEO XXII	0.75			
5349	Quat I.	2.5	12,500		.29
5349	Aza	1.7			
5347	PEO XXII	0.75	12,500		.25
5347	PEO XXIII	0.75			
5350	Aza	1.7	15,800		.32
5350	Quat I.	2.5			
951	PEO XXIII	0.75	9,050		.21
951	Aza	1.7			
960	PEO XV	0.75	11,900		.24
960	Quat XIII	2.5			
966	PEO XV	0.75	11,100		.22
966	Aza	1.7			
966	Quat XIV	2.5			
1095	PEO XV	0.75	9,500		.17
1095	Quat V	2.5			
1095	PEO XV	0.75			

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EXAMPLE 9

Use of azaindenes to stabilize emulsions to which have been added polyethylene oxides and quaternary salts

To an emulsion similar to that described in Example 1, the following were added. The coatings were exposed and processed as in Example 1, either within one day after coating (fresh), or after a period of one week at 120° F., 55 percent relative humidity.

Sample	Compound	Grams per Mole AgX	Fresh		1 wk., 120° F., 55% RH, Fog
			30/E	Fog	
3000	None		6,250	.21	.81
3005	Aza	1.7	8,250	.21	.35
3004	PEO XV	0.75	10,400	.27	.73
3009	PEO XV	0.75	9,700	.24	.42
3009	Aza	1.7			
3002	Quat IV	0.75	7,900	.24	1.90
3011	Quat IV	0.75	8,850	.21	.47
3011	Aza	1.7			
3007	PEO XV	0.75	12,200	.29	2.14
3007	Quat IV	0.75			
3014	Aza	1.7	12,800	.24	.38
3014	PEO XV	0.75			
3014	Quat IV	0.75			

EXAMPLE 10

To an emulsion similar to that employed in Example 1 was added the following. The emulsion was coated and processed as in Example 1. The example illustrates the effect of using various polyethylene oxides in the emulsions.

Sample	Compound	Grams per mole AgX	30/E	Gamma	Fog
383	None		8250	1.11	.14
384	Aza	2.0	8050	1.06	.16
386	Aza	2.0	13,100	1.18	.20
386	Quat I.	2.5			
388	Aza	2.0	12,800	.96	.18
388	PEO XVI	1.0			
390	Aza	2.0	16,500	1.23	.26
390	PEO XVI	1.0			
392	Quat I.	2.5			
392	Aza	2.0	14,400	1.12	.21
392	PEO XVII	1.0			
394	Aza	2.0	18,000	1.27	.23
394	PEO XVII	1.0			
396	Quat I.	2.5			
396	Aza	2.0	10,600	1.01	.19
396	PEO XVIII	1.0			
398	Aza	2.0	14,000	1.07	.24
398	PEO XVIII	1.0			
398	Quat I.	2.5			
8491	PEO XV	0.65	10,900	1.08	.23
8491	Aza	1.7			
8492	Aza	1.7	14,400	1.14	.29
8492	Quat VI	0.10			
441	PEO XV	0.65	7,900	1.10	.20
441	Aza	1.7			
442	Aza	1.7	10,900	1.08	.25
442	PEO XV	0.75			
443	Aza	1.7	17,700	1.29	.37
443	Quat I.	2.5			
443	PEO XV	0.75			
444	PEO XXIII	0.75	12,500	.96	.25
444	Aza	1.7			
445	Quat I.	2.5	15,800	1.03	.32
445	PEO XXIII	0.75			
361	Aza	1.7	9,900	1.15	.35
361	PEO XIX	1.5			
362	PEO XIX	1.5	10,900	1.17	.44
362	Aza	1.7			
941	Quat I.	0.5	6,000	1.18	.15
941	None		6,550	1.21	.16
942	Aza	3.0			
943	Aza	3.0	7,200	.88	.18
943	Quat VII	0.75			
944	Aza	3.0	10,200	.90	.17
944	PEO XV	0.75			
945	PEO XV	0.75	13,700	.84	.21
945	Aza	3.0			
945	Quat VII	0.75			

EXAMPLE 11

To an emulsion similar to that employed in Example 1 was added the following. The emulsion was coated and processed as in Example 1. The example further illus-

trates the use of various quaternary ammonium compounds in the emulsions.

Sample	Compound	Grams per Mole AgX	30/E	Gamma	Fog
7821	None		6,000	1.06	.15
7822	Aza	3.0	6,250	1.10	.15
7823	Quat VIII	0.75	7,700	1.04	.15
7824	PEO XX	0.75	10,200	.94	.16
7825	Quat VIII	0.75	10,400	.98	.18
4061	PEO XX	0.75	7,550	.85	.15
4062	Quat IX	0.3	12,800	1.02	.26
8501	PEO XX	0.75	9,500	.93	.20
8502	Quat X	0.75	11,400	.93	.28
141	None		5,350	1.06	.12
142	Aza	3.0	6,550	1.18	.12
143	Quat XI	0.3	7,550	.95	.12
144	PEO XX	0.75	8,850	.93	.14
145	Quat XI	0.3	10,900	1.11	.16
921	Aza	1.5	5,450	1.05	.23
922	PEO XXIII	0.75	8,650	.93	.27
923	Quat XII	0.30	7,700	.90	.26
924	PEO XXIII	0.75	9,500	.84	.30

EXAMPLE 12

To a panchromatic emulsion similar to that described in Example 1 were added the following ingredients. The coatings were exposed and processed as in Example 1.

Sample	Compound	Grams per Mole AgX	30/E Speed	Gamma	Fog
721	None		5,700	.90	.13
722	PEO XV	0.75	8,250	.78	.15
723	Aza	1.5	6,400	.86	.11
724	PEO XIX	0.75	10,200	.92	.18
725	PEO XV	0.75	10,200	.80	.15
726	PEO XIX	0.75	8,850	.78	.14
727	PEO XIX	2.25	12,500	.90	.15
728	PEO XV	0.75	10,900	.85	.16
821	None		3,200	1.20	.20
822	PEO XV	0.75	5,700	.97	.21
823	PEO XIX	0.75	7,200	.95	.25
824	PEO XIX	2.25	6,700	1.13	.32

The emulsions of Example 12 can, of course, contain the indicated quaternary ammonium compounds to further increase the light-sensitivity or additionally the other sensitizing agents referred to above prior to the examples. High contrast emulsions conventionally used in the graphic arts for half-tone work and sensitized as in Example 12 with compound XIX exhibit unusually good image quality.

The chemical sensitizing agents and other addenda which I have described may be used in various kinds of photographic emulsions. In addition to being useful in non-optically sensitized emulsions they may also be used in orthochromatic, panchromatic and X-ray 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.

The dispersing agent for the silver halide may be gelatin or other colloidal material such as collodion, albumin, cellulose derivatives or synthetic resins.

It will be understood that I contemplate as included within my invention all modifications and equivalents falling within the scope of the appended claims.

What I claim is:

1. A light-sensitive silver halide emulsion sensitized with a mixture of an alkylene oxide polymer selected from the class consisting of (1) polyalkylene ether glycols and (2) condensation products of an alkylene oxide with organic compounds containing an active hydrogen atom, said alkylene oxide containing from 2 to 4 carbon atoms and said alkylene oxide polymer having a molecular weight of at least 300, and a mono-quaternary ammonium salt silver halide chemical sensitizing agent having a chain of at least seven atoms attached to a single quaternary ammonium group.

2. A light-sensitive silver halide emulsion sensitized with a mixture of an alkylene oxide polymer selected from the class consisting of (1) polyalkylene ether glycols and (2) condensation products of an alkylene oxide with organic compounds containing an active hydrogen atom, said alkylene oxide containing from 2 to 4 carbon atoms and said alkylene oxide polymer having a molecular weight of at least 300, and a mono quaternary ammonium salt silver halide chemical sensitizing agent having an alkyl chain of at least seven atoms attached to a single quaternary ammonium group.

3. A light-sensitive silver halide emulsion sensitized with a mixture of an alkylene oxide polymer selected from the class consisting of (1) polyalkylene ether glycols and (2) condensation products of an alkylene oxide with organic compounds containing an active hydrogen atom, said alkylene oxide containing from 2 to 4 carbon atoms and said alkylene oxide polymer having a molecular weight of at least 300, and a mono quaternary ammonium salt silver halide chemical sensitizing agent having a chain of at least seven atoms attached to a single quaternary ammonium group, the emulsion further containing an azaindene as a fog-inhibiting agent.

4. A light-sensitive silver halide emulsion sensitized with a mixture of an alkylene oxide polymer selected from the class consisting of (1) polyalkylene ether glycols and (2) condensation products of an alkylene oxide with organic compounds containing an active hydrogen atom, said alkylene oxide containing from 2 to 4 carbon atoms and said alkylene oxide polymer having a molecular weight of at least 300, and a mono quaternary ammonium salt silver halide chemical sensitizing agent having an alkyl chain of at least seven atoms attached to a single quaternary ammonium group, the emulsion further containing an azaindene as a fog-inhibiting agent.

5. The emulsion of claim 1 wherein the quaternary ammonium salt is a tetraalkyl quaternary ammonium salt.

6. The emulsion of claim 1 wherein the quaternary ammonium salt is one having a quaternary nitrogen atom which is a part of a ring system.

7. The emulsion of claim 1 wherein the alkylene oxide polymer is an ethylene oxide polymer.

8. The emulsion of claim 1 wherein the alkylene oxide polymer is a polyethylene oxide oleyl ether.

9. A light-sensitive silver halide emulsion sensitized with a mixture of an ethylene oxide polymer having a molecular weight of at least 300, and a member of the class consisting of laurylpyridinium perchlorate, laurylpyridinium-p-toluene sulfonate, hexadecylpyridinium bromide, N-n-tetradecyl-N-methylmorpholinium-p-toluene sulfonate, lauryl trimethylammonium-p-toluene sulfonate, and n-myristyl trimethylammonium-p-toluene sulfonate.

10. The emulsion of claim 9 further containing an azaindene as a stabilizing agent.

11. The emulsion of claim 2 wherein the alkylene oxide polymer is an ethylene oxide polymer.

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12. The emulsion of claim 3 wherein the alkylene oxide polymer is an ethylene oxide polymer.

13. A light-sensitive silver halide emulsion sensitized with a mixture of an ethylene oxide polymer having a molecular weight of at least 300 and a monoquaternary ammonium salt silver halide chemical sensitizing agent having a chain of at least seven atoms attached to a single quaternary ammonium group, and containing a stabilizing agent of the class consisting of aminotriazaindenes, aminotetrazaindenes, aminopentazaindenes, hydroxytriazaindenes, hydroxytetrazaindenes, and hydroxypentazaindenes.

14. A light-sensitive silver halide emulsion sensitized with a mixture of an alkylene oxide polymer of the class consisting of (1) a polyalkylene ether glycol and (2) a condensation product of an alkylene oxide with an organic compound containing at least one active hydrogen atom in

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a radical of the class consisting of hydroxy, amino, mercapto, carboxyl, amido and methylene, said alkylene oxide polymer having a molecular weight of at least 300, and a monoquaternary ammonium salt silver halide chemical sensitizing agent having a chain of at least seven atoms attached to a single quaternary ammonium group.

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