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3,294,540

LITH-TYPE EMULSIONS WITH BLOCK CO-POLYMERS

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2 Sheets-Sheet 1

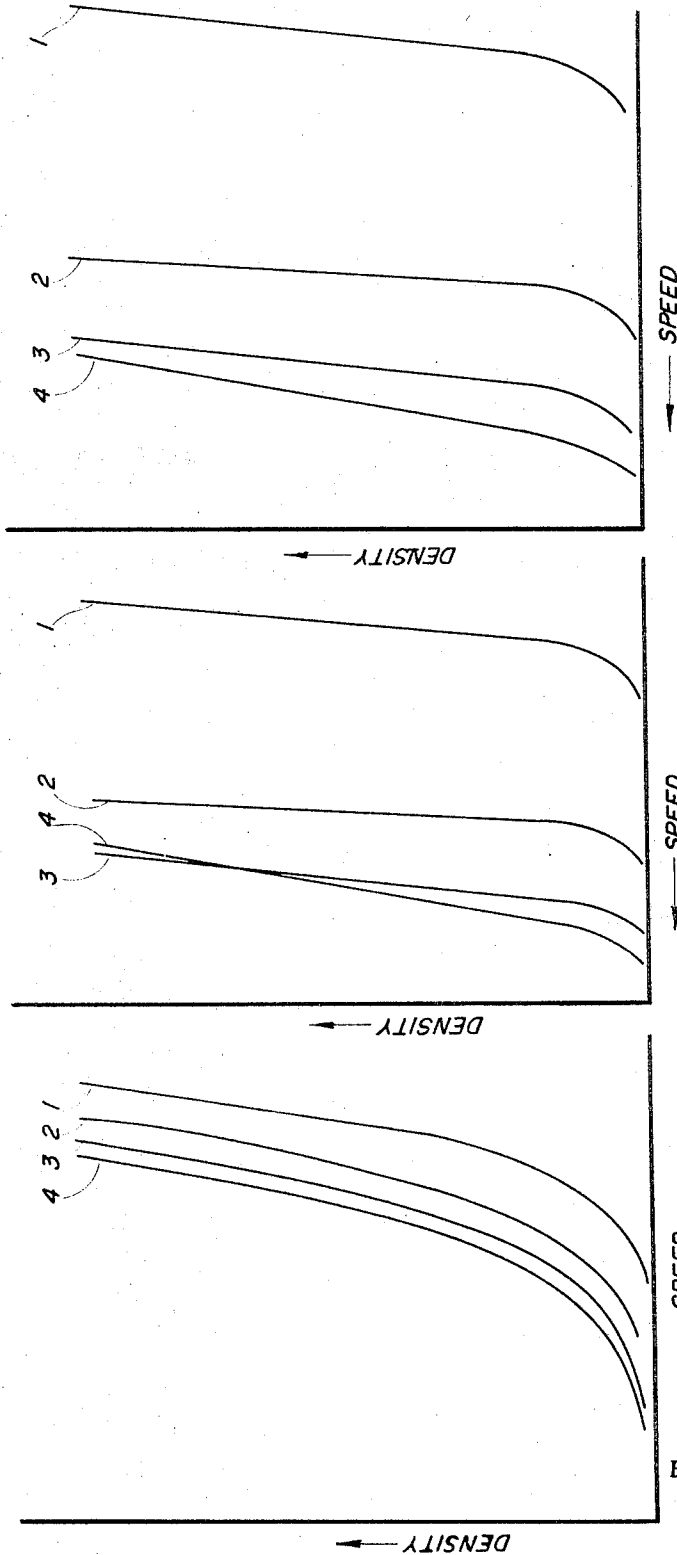


FIG. 3

FIG. 2

FIG. 1

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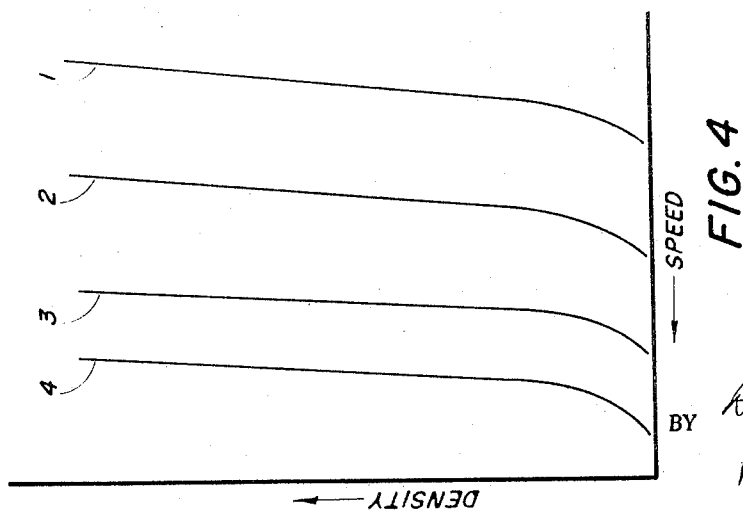
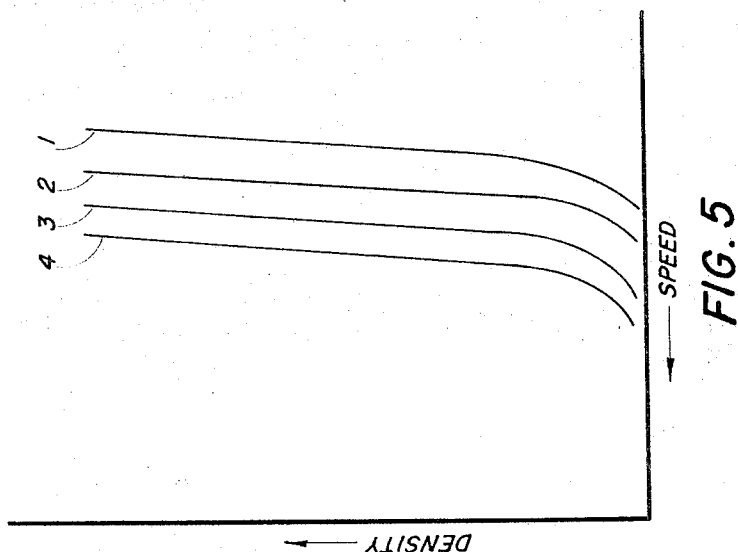
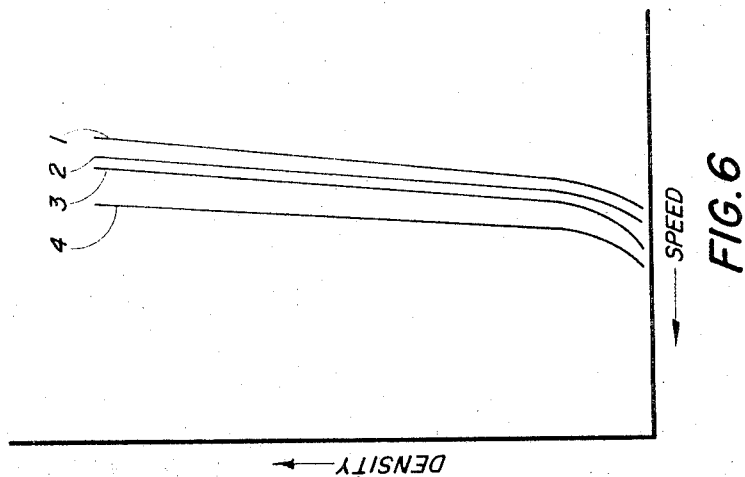
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3,294,540 LITH-TYPE EMULSIONS WITH BLOCK CO-POLYMERS

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12 Claims. (Cl. 96—87)

This invention relates to photography and particularly to improved photographic silver halide emulsions of the "lith-type."

Photographic films used in the graphic arts for making half-tone or line images should be capable of producing extremely high contrast and good image sharpness. These factors contribute in the case of half-tone images to high "dot quality," that is, to the production of half-tone dots of high density and sharpness.

The photographic elements of the "lith-type," that is, elements that have a fine grain high contrast silver halide emulsion containing at least 60 mole percent chloride, less than 40 mole percent bromide and less than about 5 mole percent iodide, require the use of pure hydroquinone developer solutions having very low free sulfite ion concentration in the alkaline solution in order to produce the high contrast and high dot quality required for good quality half-tone reproduction. Such developer solutions are unstable, having very short tray or tank life after exposure to air, so that the solutions must be mixed fresh just before they are to be used for processing and then discarded.

In many instances the films and processes available do not produce the desired latitude and have the desired ease in exposing and processing the film to produce the required quality. This has resulted from the contrast of the image reproduction in the photographic elements being overly sensitive to development time, and from a non-linearity in the relationship between the film speed and development time, causing unequal increases in film speed from equal increases in development time.

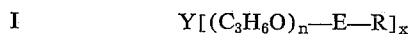
It is therefore an object of my invention to provide a photographic film which produces high contrast and high quality images even when developed with a developer solution having relatively high free-sulfite content that has good stability upon prolonged exposure to air in tray or tank. Another object is to provide a photographic element which is capable of producing high contrast, high quality half-tone images over a relatively broad range of film exposure and development times. Another object is to provide a photographic element which has good evenness of development. Still other objects will become apparent from the following specification and claims.

These and other objects are accomplished according to my invention by use of a photographic light sensitive element comprising a support, at least one hydrophilic colloid layer containing a very fine grain photographic silver halide emulsion having at least 60 mole percent chloride, less than 40 mole percent bromide and less than about 5 mole percent iodide, and at least one hydrophilic colloid layer containing certain water-soluble block polymers of polyoxypropylene and polyoxyethylene such that the block polymer is contiguous with the silver halide. The water-soluble block polymers used in photographic elements according to my invention include those block polymers in which the polyoxypropylene chain (or moiety) has an average molecular weight between 800 and 3,000 and in which the polyoxyethylene units consti-

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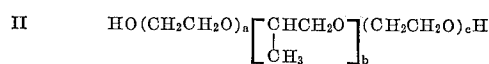
tute from about 10 to about 70 percent by weight of the polymer. The image reproductions produced in my "lith-type" emulsion layers are of excellent quality. Although the conventional alkaline, pure hydroquinone, low free-sulfite developer may be used to develop my exposed elements, it is also advantageous to use a developer having from 10 to about 30 grams of an alkali sulfite per liter of the developer solution. When my elements are developed in the preferred developer solutions not only is the image contrast high and the dot quality excellent but this excellent quality is produced over a wide range of exposures and development times.

The water-soluble block polymers of polyoxypropylene and polyoxyethylene used to advantage according to my invention include those represented by the formula:



wherein Y represents an organic radical having a valence of x , said radical being the residue of an organic compound containing atoms selected from the class consisting of carbon, hydrogen, oxygen, nitrogen and sulfur with x active hydrogen atoms, such as, the residue of polyhydroxy compounds, e.g., ethylene glycol, 1,2-propanediol, 1,5-pentanediol, 1,2,3-propanetriol, sucrose, etc., the residue of a polybasic acid, e.g., oxalic acid, malonic acid, succinic acid, maleic acid, citric acid, etc., the residue of a polyamine, e.g., ethylenediamine, 1,3-diaminopropylene, etc., the residue of a polyamide, e.g., malonamide, succinamide, etc., the residue of a polythiol, e.g., 1,2-ethylenedithiol, 1,3-propylenedithiol, etc.; n is an integer greater than 1; x is an integer greater than 1, so that the values of n and x are such that the molecular weight of the said polymer exclusive of Y, E and R is between 800 and 3,000; E represents a polyoxyethylene chain constituting from about 10 to about 70 percent by weight of said block polymer; and R represents the hydrogen atom, an alkyl group having from 1 to 20 carbon atoms (such as methyl, propyl, decyl, dodecyl, octadecyl, etc.), an alkyl carbonyl group in which the alkyl group has from 1 to 20 carbon atoms as described above, an aryl carbonyl group, such as, benzoyl, p-methyl benzoyl, etc.

Included among the preferred block polymers are those having the formula:



in which b represents an integer of from 14 to 52; a and c are each integers such that the sum of $a+c$ has a total of from 4 to 48 and the polyoxyethylene groups constitute between 10 and 70 percent by weight of the block polymer.

The block polymers of Formula II and of Formula I where R represents the hydrogen atom are described in Lundstedt U.S. Patent 2,674,619, issued April 6, 1954, and Lundstedt U.S. Patent 3,022,335, issued February 20, 1962. The block polymers of Formula I in which R is hydrogen are readily converted to compounds where R represents an organic residue by reaction with the appropriate reagent in a suitable inert organic solvent that is preferably anhydrous. For example, alkyl halides, such as alkyl chlorides, alkyl bromides, etc., are used to advantage to replace the terminal hydrogen atom of the block polymer with an alkyl group. Alkyl-p-toluenesulfonates are also used to advantage to place an alkyl group on the end of the block polymers. The appropriate acid chloride or acid anhydride, such as, acetyl chloride, propionyl

chloride, stearoyl chloride, benzoyl chloride, acetic anhydride, etc., are used to advantage to prepare block polymers of Formula I in which R is an alkyl carbonyl or an aryl carbonyl group. These reactions are well known to those skilled in the art. Many of the block polymers of Formulas I and II are available commercially.

My photographic elements coated with a "lith-type" emulsion containing my block polymers of polyoxypropylene and polyoxyethylene are valuable for use in graphic art reproduction. My elements are particularly valuable when developed with a dihydroxybenzene developer with a high free sulfite ion concentration in an alkaline solution. My elements provide the following advantages:

(1) More even rate of speed change with changes in development time which allows varying the development time systematically to control speed without sacrificing quality;

(2) Better "dot quality" over a wider range of development times and temperatures;

(3) Elimination of or reduction in development defects, such as, "drag lines" when the materials are developed in automatic roller transport processing equipment;

(4) High contrast and much better dot quality when stable developer solutions containing a high free-sulfite concentration, e.g., 10 to 30 grams of an alkali metal sulfite per liter of solution are used;

(5) Increased speed without loss of dot quality when an onium salt is incorporated in my light-sensitive emulsion layer, and still further advantages will be apparent from the specification and claims.

It is unexpected that the immediate block polymers would produce these advantages since closely related block polymers of polyoxypropylene and polyoxyethylene that are outside my invention produce images having low contrast, low dot quality and unevenness of development.

The quality of the silver images produced in "lith-type" emulsion layers is conveniently measured in terms of contrast (i.e., γ) and dot quality. Photographic image contrast is the slope of the straight line portion of a graph of optical density of the image vs. log of exposure. Dot quality is a measure of the quality of the reproduction of a half-tone image. "Lith-type" photographic elements exposed to a half-tone image, and developed, produce areas commonly referred to as shadow dots and areas known as highlight areas. Intermediate between these two extremes are areas of varying size. The dot quality used herein is a measure of the areas referred to as 50% dots (i.e., $\frac{1}{2}$ clear and $\frac{1}{2}$ developed density) and is expressed in a progressive scale where "9" is excellent and "1" is extremely poor. A 50% dot quality below "6" is generally not acceptable.

The factor "evenness of development" is explained in connection with Example 1 later in the specification.

Included among the block polymers used to advantage according to my invention are the following typical polymers used for illustrative purposes.

Block Polymer No.	Y Group derived from—	Average Value of γ in Formula I	Percent polyoxyethylene by weight of Block polymer
1.-----	1,2-propanediol-----	30	10
2.-----	do-----	30	20
3.-----	do-----	22	40
4.-----	do-----	30	50
5.-----	do-----	30	40
6.-----	do-----	47	20
7.-----	do-----	39	10
8.-----	1,5-pentanediol-----	24	50
9.-----	1,2,3-propanetriol-----	36	48
10.-----	Ethylenediamine-----	32	50

These block polymers are available commercially under the tradename Pluronic. Block polymers 1 through 7 are sold under the trade name Pluronic L61, L62, L44, P65, L64, L92 and L81, respectively.

The block polymers used according to my invention are water soluble and are advantageously added in a water

solution to the aqueous hydrophilic colloid (either with or without the silver halide) before it is coated. The block polymers are used to advantage over a wide range of concentrations. The operable range of concentrations is from .001 to 1.00 gram of block polymer per mole of silver, while the preferred range is from 0.010 to 0.200 gram per mole of silver. The optimum concentration of a given block polymer used in my elements depends upon the results desired, the particular silver halide emulsion, the developer solution, etc., and is readily determined by methods well known in the art. The determination of the optimum concentration is preferably made by employing the block polymer in the silver halide emulsion layer or in an adjacent hydrophilic colloid layer according to the element that is desired.

The fine grain silver halide emulsions used to advantage have silver halide crystals preferably containing at least 60 mole percent chloride, less than 40 mole percent bromide and less than about 5 mole percent iodide. The emulsions can be prepared as described by MacWilliam U.S. 2,756,148, issued July 24, 1956. These emulsions may be used without being sensitized, however, it is advantageous to spectrally sensitize them according to methods well known in the art to make them ortho-sensitized or panchromatically-sensitized.

The silver halide is dispersed in hydrophilic colloid materials used as binders, including gelatin, collodion, gum arabic, cellulose ester derivatives, such as, alkyl esters of carboxylated cellulose, hydroxy ethyl cellulose, carboxy methyl hydroxy ethyl cellulose, synthetic resins, such as the amphoteric copolymers described by Clavier et al. in U.S. Patent 2,949,442, issued August 16, 1960, polyvinyl alcohol, and others well known in the art. Examples of these polymeric gelatin substitutes are copolymers of allylamine and methacrylic acid; copolymers of allylamine, acrylic acid and acrylamide; hydrolyzed copolymers of allylamine, methacrylic acid and vinyl acetate; the copolymers of allylamine, acrylic acid and styrene; the copolymers of allylamine, methacrylic acid and acrylonitrile; alkyl acrylate—acrylic acid copolymers, e.g., copolymers of butyl acrylate—acrylic acid, etc.

When my block polymers are incorporated in a layer adjacent to the silver halide emulsion layer instead of in the light-sensitive layer, any of the hydrophilic colloids described hereinbefore may be used to advantage as a binder for coating my polymers.

It is advantageous to add certain onium salts, such as, quaternary ammonium salts, sulfonium salts and phosphonium salts to my light-sensitive emulsions in order to increase the photographic speed without adversely affecting the improved dot quality, contrast and evenness of development. Examples of quaternary ammonium salts include nonyl pyridinium perchlorate, hexoxymethyl pyridinium perchlorate, ethylene bis-dioxymethyl pyridinium perchlorate and others described by Carroll U.S. 2,271,623, issued February 3, 1942, hexadecamethylene-1,16-bis(pyridinium perchlorate), 9,16-diaza-7,18-dioxo-8,17 - dioxotetracosane-1,24-bis(pyridinium perchlorate), and others of Beavers et al. U.S. 2,944,898, issued July 12, 1960. Other examples include the onium salts of polyoxyalkylenes of Carroll et al. U.S. 2,944,902, issued July 12, 1960, the polyonium salts of Carroll et al. U.S. 2,288,226, issued June 30, 1942, such as bis(lauryl methyl sulfonium p-toluene sulfonate) 1,2-ethane, N,N'-tri-methylene dioxymethyl pyridinium perchlorate etc., the sulfonium salts of Carroll et al. U.S. 2,275,727, issued March 10, 1942, such as, n-decyl dimethyl sulfonium p-toluene sulfonate, n-nonyl dimethyl sulfonium p-toluene sulfonate, etc., and the phosphonium salts of Carroll et al. U.S. 2,271,622, issued February 3, 1942, such as, tetramethylene bis-triethyl phosphonium bromide, lauryl-triethylphosphonium bromide, etc.

My light-sensitive emulsions can be coated to advantage on any of the conventional photographic supports, including glass, cellulose acetate, polystyrene, polyalkyl-

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eneterephthalate, etc. The block polymers can be coated advantageously in the silver halide emulsion layer, or in a hydrophilic colloid layer that is either under or over the silver halide emulsion layer so that the block polymer is contiguous to the silver halide.

My invention is still further illustrated by the following examples.

Example 1

A gelatino silver chlorobromiodide emulsion containing approximately 90 mole percent chloride, 9 mole percent bromide, and 1 mole percent iodide was divided into separate portions and the polymer or copolymer indicated in Table I was added to the individual portions. The resulting compositions were coated on separate pieces of a polyalkyleneterephthalate film support at a coverage of 455 mg. of silver and 450 mg. of gelatin per square foot. Samples of each coating were exposed on an intensity scale sensitometer and processed in a developer of the composition:

Hydroquinone	15.0
Sodium formaldehyde bisulfite	50.0
Sodium carbonate	35.0
Sodium bicarbonate	22.5
Sodium sulfite	2.5
Potassium bromide	0.75
Water to make 1.0 liter.	

for 4¾ minutes, fixed in a conventional sodium thiosulfate fixing bath, washed and dried. The polymer or copolymer composition, concentration in each coating are listed with the relative speed, contrast (i.e., γ), dot quality of the developed coating and the evenness of development that were obtained are summarized in Table I.

TABLE I

Photographic element	Polymer	Molecular weight of polyoxypropylene block	Percent polyoxyethylene	Grams of polymer per mole of silver	Relative speed	γ	Dot quality	Evenness of development
1	PEO*		100	.05	126	6.4	1	.08
2	PEO*		100	.10	123	5.0	1	.14
3	PEO*		100	.15	105	9.0	3	.18
4	PEO*		100	.20	89	13.0	4	.44
5	PEO*		100	.20	82	13.2	5	.21
6	1	1,750	10	.045	55	10.0	8	.03
7	2	1,750	20	.06	16	10.2	8	.04
8	3	1,200	40	.02	55	11.5	8	.04
9	4	1,750	50	.05	62	12.0	7	.13
10	5	1,750	40	.045	30	11.0	8	.04
11	6	2,750	20	.23	40	11.2	8	.02
12	A	3,250	40	.10	73	5.7	3	.24
13	B	1,750	80	.05	138	2.4	3	.14

*PEO=Oleyl ether of polyethylene oxide, average M.W.=1,500.

The polymer PEO is the oleyl ether of polyethylene oxide having an average molecular weight of 1500. Block polymers A and B have polyoxypropylene units and polyoxyethylene units but are outside of the invention. Copolymers 1, 2, 3, 4, 5 and 6 have been described previously.

The data in Table I show that my "lith" elements containing block polymers 1, 2, 3, 4, 5 and 6 produced good image contrasts of from 10 to 12, good dot quality ranging from 7 to 8 and good evenness of development indicated by a value from .02 to .13. The elements outside my invention containing PEO produced very poor to unacceptable dot quality and very poor evenness of development. Similarly elements containing block polymers A or B produced very low contrast images, very poor dot quality and poor evenness of development.

Ideally, the rate of change in the log of the speed with change in development time should equal a constant; that is:

$$\log \text{ speed at time } [t+1] - \log \text{ speed at time } t = K$$

When the rate of change in the speed is plotted against

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the development time, the slope of the resultant curve will approach 0 as K approaches a constant value. Evenness of development is the slope of the plot of K against time. In the above table, evenness of development is expressed in this way. The smaller the number, the more even the development. This value indicates the even spacing between the sensitometric curves for equal differences in development time.

The accompanying drawings FIGS. 1, 2, 3, 4, 5 and 6 which show plots of image density vs. speed will further illustrate my invention. Each figure shows 4 curves, curve 1 for 1¾ minute development, curve 2 for 2¾ minute development, curve 3 for 3¾ minute development and curve 4 for 4¾ minute development.

FIG. 1 shows curves 1 through 4 for a control "lith" element.

FIG. 2 shows curves 1 through 4 for a "lith" element outside my invention containing polyoxyethylene.

FIG. 3 shows curves 1 through 4 for a "lith" element outside my invention containing block polymer A described previously.

FIG. 4 shows curves 1 through 4 for my "lith" element containing my block polymer No. 3.

FIG. 5 shows curves 1 through 4 for my "lith" element containing my block polymer No. 5.

FIG. 6 shows curves 1 through 4 for my "lith" element containing my block polymer No. 7.

The curves of FIG. 2 show that when polyoxyethylene is added to a "lith" emulsion to increase the contrast and improve dot quality, the curve spacing (i.e., evenness of development) is erratic. Similarly, FIG. 3 shows that a "lith" emulsion containing block polymer A outside my invention has erratic curve spacing. However, as

shown by FIG. 4 when a "lith" emulsion contains one of my block polymers such as No. 3 the curve spacing is more regular indicating good evenness of development which is a distinct advantage, since it allows one to vary the speed of the material at a constant rate by varying the development time without sacrificing contrast or dot quality.

By varying the concentration of my block polymer or by using block polymers having polyoxypropylene chains having relatively high molecular weights it is also possible to make "lith" elements giving relatively small changes in speed with development time. This characteristic is particularly advantageous in automatic processing equipment where the activity of the developer may vary with aging, or other variables may be present which affect the development rate. The following will serve to illustrate this advantage.

Example 2

Coatings were made and processed as in Example 1 for the polymer indicated in Table II. Development times of 1¾, 2¾, 3¾ and 4¾ minutes were used. The changes

in relative speed over 3 minutes development were determined and listed below.

TABLE II

Polymer	Molecular weight of polyoxypropylene	Percent polyoxyethylene	Grams of polymer per mole of silver	Change in relative speed over 3 minutes development
Oleyl ether of POE, M.W. 1,500		100	0.12	561
No. 3	1,200	40	0.02	289
No. 5	1,750	40	0.035	100
No. 7	2,250	10	0.50	35

This effect can be more clearly seen by noting the closer spacing of curves 1 through 4 in FIG. 6 than in FIG. 5.

Example 3

A very fine grain high contrast gelatino silver chlorobromide emulsion in which 70 percent of the halide was the chloride was prepared and divided into three equal portions. One portion was used as a control. Oleyl ether of polyoxyethylene (molecular weight 1540) was added to the second portion and stock polymer No. 2 was added to the third portion of the emulsion as indicated in Table III. These emulsions were coated, exposed and developed as described in Example 1 but using a very low free-sulfite developer having the composition:

Sodium sulfite, desiccated	G. 30.0
Paraformaldehyde	7.5
Sodium bisulfite	2.2
Boric acid, crystals	7.5
Hydroquinone	22.5
Potassium bromide	1.6
Water to make 1.0 liter.	

The results are summarized in the following table.

TABLE III

Polymer	Gm. polymer per mole Ag	Relative speed	γ	Fog	Dot quality
None		100	5.1	.01	1
Oleyl ether of PEG 1540	0.5	72	9.1	.01	5
Block Polymer No. 2	0.125	49	9.5	.01	9

The results clearly show that my block polymer No. 2 produces excellent dot quality at a high contrast while the oleyl ether of PEG 1540 produces poor dot quality.

Example 4

The polymers indicated in Table IV were added to separate portions of a silver chlorobromoidide emulsion containing approximately 90 mole percent chloride, 9 mole percent bromide and 1 mole percent iodide. Coatings made of these emulsions, as described in Example 1, were given a 1¾ minutes' development in a high free-sulfite "lith" developer having the composition:

Hydroquinone	g-- 15.0
Boric acid	g-- 5.5
Potassium bromide	g-- 2.7
Potassium carbonate	g-- 90.0
Potassium sulfite	g-- 20.0
Diethylene glycol	cc-- 30.0
Water to make 1000.0 cc.	

The results summarized in Table IV show the better quality obtained with my polymers No. 3 and No. 2 compared to a simple PEO having a molecular weight of 1540.

TABLE V

Polymer	Gm. polymer per mole of silver	Relative speed	γ	Dot quality
PEO	.120	100	7.0	5
No. 3	.03	42	13+	8
No. 2	.045	105	12.5	7

The following example will serve to illustrate that the speed of my "lith" emulsions can be increased by adding an onium salt to the emulsion without adversely affecting the improved dot quality and contrast obtained from the addition of a preferred block polymer.

Example 5

A high contrast silver chlorobromide emulsion containing 0.02 gram of my block polymer No. 3 per mole of silver halide was divided into two portions. One portion was coated on a support as it was and to the other portion was added 0.66 gram of N,N'-ethylenedioxyethylene pyridinium perchlorate per mole of silver before it was coated. The strips were exposed, developed, fixed, washed and dried as described in Example 1 but given only 2¾ minutes' development. The relative speed, γ and dot quality are summarized in Table V.

TABLE V

Onium Salt	Grams per mole silver	Relative speed	γ	Dot quality
None		100	6.1	9
N,N'-ethylenedioxyethyl pyridinium perchlorate	.066	151	7.9	9

Similarly, other quaternary ammonium salts, sulfonium salts and phosphonium salts as disclosed previously can be used to advantage with other block polymers of my invention.

My "lith" elements coated with fine grain high contrast silver halide emulsions containing at least 60 mole percent chloride, less than 40 mole percent bromide and less than about 5 mole percent iodide contain certain water-soluble block polymers of polyoxypropylene and polyoxyethylene. The block polymer is incorporated in the light-sensitive layer or in a layer adjacent to the light-sensitive layer so that the polymer and silver halide are contiguous. The block polymers used to advantage according to my invention include those in which the polyoxypropylene chain has an average molecular weight between 800 and 3000, and in which the polyoxyethylene units constitute from about 10 to about 70 percent by weight of the block polymer. My elements give high contrast images with high dot quality and good evenness of development with "lith" developer solutions. My elements are particularly valuable because they produce these high quality image reproductions even when stable high free-sulfite developer solutions are used. Since "lith" elements containing simple polyoxyethylene and certain block polymers of polyoxypropylene and polyoxyethylene that are outside my invention produce low contrast and poor dot quality, it is unexpected that my elements containing my block polymers produce the high quality images that characterize them, especially with the stable high free-sulfite developer solutions.

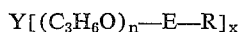
The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A light-sensitive photographic element comprising a support coated with at least one hydrophilic colloid layer containing a silver halide emulsion in which the chloride comprises at least 60 mole percent of the halide, and at

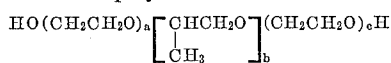
least one hydrophilic colloid layer containing a water-soluble block polymer of polyoxypropylene and polyoxyethylene in which the polyoxypropylene moiety has an average molecular weight between 800 and 3,000 and the polyoxyethylene units constitute from about 10 to about 70 percent by weight of said polymers, such that the said block polymer is contiguous to the said silver halide.

2. A photographic element of claim 1 in which the water-soluble block polymer has the formula:



wherein Y represents an organic radical having a valence of X; n is an integer; x is an integer greater than 1, so that the values of n and x are such that the molecular weight of the said polymer exclusive of Y, E and R is between 800 and 3,000; E represents a polyoxyethylene chain constituting from about 10 to about 70 percent by weight of said polymer; and R is a member selected from the class consisting of the hydrogen atom, an alkyl group, an alkyl carbonyl group, and an aryl carbonyl group.

3. A photographic element of claim 1 in which the water-soluble block polymer has the formula:



wherein b represents an integer of from 14 to 52; and a and c each represent integers such that the sum of a+c represents an integer of from 4 to 48 and the polyoxyethylene groups constitute between 10 and 70 percent by weight of said polymer.

4. A photographic element of claim 1 in which the water-soluble block polymer and the silver halide emulsion are in the same hydrophilic colloid layer.

5. A photographic element of claim 1 in which the water-soluble block polymer is in a hydrophilic colloid layer coated over the hydrophilic colloid layer containing the silver halide emulsion.

6. A photographic element of claim 1 in which the water-soluble block polymer is in a hydrophilic colloid layer coated under the hydrophilic colloid layer containing the silver halide emulsion.

7. A photographic element of claim 1 in which the light-sensitive layer contains an onium salt selected from the class consisting of a quaternary ammonium salt, a sulfonium salt and a phosphonium salt.

8. A photographic element comprising a transparent support coated with a light-sensitive layer comprising:

- (a) gelatin;
- (b) a silver chlorobromiodide emulsion containing approximately 90 mole percent chloride, approximately 9 mole percent bromide and approximately 1 mole percent iodide; and
- (c) a water-soluble block polymer comprising a water-insoluble polyoxypropylene chain having water-soluble polyoxyethylene groups at each end of said polyoxypropylene chain in which the molecular weight of the polyoxypropylene chain is 1750 and the polyoxyethylene groups constitute 10 percent by weight of said copolymer.

9. A photographic element comprising a transparent support coated with a light-sensitive layer comprising:

- (a) gelatin;
- (b) a silver chlorobromiodide emulsion containing approximately 90 mole percent chloride, approximately 9 mole percent bromide and approximately 1 mole percent iodide; and

(c) a water-soluble block polymer comprising a water-insoluble polyoxypropylene chain having water-soluble polyoxyethylene groups at each end of said polyoxypropylene chain in which the molecular weight of the polyoxypropylene chain is 1750 and the polyoxyethylene groups constitute 20 percent by weight of said polymer.

10. A photographic element comprising a transparent support coated with a light-sensitive layer comprising:

- (a) gelatin;
- (b) a silver chlorobromiodide emulsion containing approximately 90 mole percent chloride, approximately 9 mole percent bromide and approximately 1 mole percent iodide; and
- (c) a water-soluble block polymer comprising a water-insoluble polyoxypropylene chain having water-soluble polyoxyethylene groups at each end of said polyoxypropylene chain in which the molecular weight of the polyoxypropylene chain is 1200 and the polyoxyethylene groups constitute 40 percent by weight of said polymer.

11. A photographic element comprising a transparent support coated with a light-sensitive layer comprising:

- (a) gelatin;
- (b) a silver chlorobromiodide emulsion containing approximately 90 mole percent chloride, approximately 9 mole percent bromide and approximately 1 mole percent iodide; and
- (c) a water-soluble block polymer comprising a water-insoluble polyoxypropylene chain having water-soluble polyoxyethylene groups at each end of said polyoxypropylene chain in which the molecular weight of the polyoxypropylene chain is 1750 and the polyoxyethylene groups constitute 40 percent by weight of said polymer.

12. A photographic element comprising a transparent support coated with a light-sensitive layer comprising:

- (a) gelatin;
- (b) a silver chlorobromiodide emulsion containing approximately 90 mole percent chloride, approximately 9 mole percent bromide and approximately 1 mole percent iodide; and
- (c) a water-soluble block polymer comprising a water-insoluble polyoxypropylene chain having water-soluble polyoxyethylene groups at each end of said polyoxypropylene chain in which the molecular weight of the polyoxypropylene chain is 2750 and the polyoxyethylene groups constitute 20 percent by weight of the said polymer.

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