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WATER-SOLUBLE POLYOXYALKYLENATED BUTYNE-2-DIOL-1,4 DEVELOPMENT ACCELERATORS

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The present invention relates in general to photographic developers and more particularly to photographic developers having an exceptional capacity to markedly improve the sensitometric characteristics, e.g., effective speed, of photographic materials developed therewith.

Photographic film materials currently available commercially for the most part possess the requisite speed as well as fineness of grain to satisfy the normal requirements of the vast majority of users. As is well known, however, the sensitometric properties of a given photographically-sensitized material are determined essentially by two factors, namely, the intensity of the exposure to which the material is subjected, as well as the maximum density obtainable by development of the film, the latter depending in turn on the manner in which the film is developed as well as the nature of the ingredients included in the developer composition. Accordingly, if two samples of the same film material are subjected to identical exposures and one is processed in a mildly energetic developer while the other is processed in a high energy developer, each to an equivalent gamma, it may be said in general that the second case will result in a higher emulsion speed than that of the first case.

The so-called high energy developers heretofore provided, i.e., those which yield maximum density levels in reduced periods of development time have, in many instances, provided only marginal advantage over the more mildly acting developer compositions. While enabling the attainment of substantially reduced development times, the high speed developers currently known, in many instances, pose serious problems such as excessive fog and graininess, as well as a general softening in the photographic emulsion developed therewith. The effect of fogging, of course, is to increase the overall density of the negative obtained and to depress the contrast of the image in the less exposed areas. As a general rule, the fogging density produced is greater in the case of high speed emulsions and becomes more pronounced with increased development time and/or temperature. Consequently, considerable difficulty is often encountered in obtaining proper gradation and especially within the time interval prescribed for development.

In explanation of the foregoing, it has been postulated that the principal development action involved appears to be at the surface portions of the exposed layer, due, probably, to the resistance of the gelatin emulsion to penetration by the developer solution. Increasing the developing time in order to promote deeper penetration into the exposed layer, as would be the case with the more mildly acting developer solutions, has likewise proved unsatisfactory, since there invariably results a significant increase in the fog characteristics. In addition, the unduly prolonged developing times required with the use of mildly acting developer solutions to a great extent vitiates their commercial feasibility.

In an effort to overcome or otherwise alleviate the foregoing and related problems, the art has resorted to the practice of providing photographic developer solutions with certain chemical compounds, i.e., accelerators, antifoggants, stabilizers, etc. It has been suggested, for example, that the addition of polyethylene glycols, as well

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as certain functional derivatives thereof to aqueous developer solutions, achieves a significant decrease in the induction period required for development. As examples of further compounds suggested for use in a similar relationship, i.e., as development accelerators, there may be mentioned the guanazoles, certain water-soluble inorganic salts, various bispyrrolidinium salts, hydrazines, a variety of substituted ureas and thioureas, water-soluble ammonium salts, and the like. Although providing some measure of improvement, compounds of the foregoing type have, nevertheless, proved unsatisfactory in a number of important respects. While they often yield optimum density levels in reduced development times, perhaps their principal shortcoming relates to their failure to eliminate fog and graininess to an acceptable extent. Moreover, such compounds have been found to require relatively stringent conditions for effective use. For example, their concentration must be controlled within rather precise limits, since relatively minor variations in their amounts often vitiate their overall effectiveness with the result, in some cases, that the effective speed of the photographic silver halide emulsion may actually be reduced.

In any event, none of the chemical accelerators thus far provided has been found to be capable of producing an increase in speed beyond the optimum speed inherent in the photographic emulsion or which results from the nature of the developer employed.

Thus, a primary object of the present invention resides in the provision of improved photographic developers wherein the above disadvantages are eliminated or at least mitigated to a substantial degree.

Another object of the present invention resides in the provision of improved photographic developers possessing outstanding speed and fine-grain characteristics.

A further object of the present invention resides in the provision of improved developer compositions which exhibit little or no tendency to fog silver halide emulsions developed therewith.

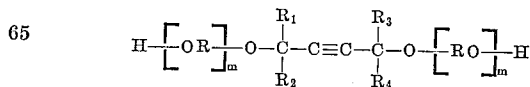
A still further object of the present invention resides in the provision of improved developer compositions characterized by a significant decrease in the induction period required for photographic development therewith.

Further objects of the present invention will become apparent hereinafter as the description thereof proceeds.

The attainment of the foregoing and related objects is made possible in accordance with the present invention which in its broader aspects is based upon the discovery that silver halide developer compositions can be synergistically modified to advantage by incorporating therein a small amount of a water-soluble polyoxyalkylenated derivative of 1,4-butyne diol.

One of the truly outstanding features characterizing the discovery forming the basis of the present invention, relates to the fact that developer compositions modified in accordance therewith enable the attainment of effective film speeds substantially in excess, i.e., on the order of 50% and higher of the optimum speed ordinarily obtainable by virtue of the particular silver halide emulsion and/or developer employed.

The 1,4-butyne diol polyoxyalkylenated derivatives contemplated for use in accordance with the present invention can be conveniently represented according to the following structural formula:



wherein R represents ethylene or propylene and R₁, R₂, R₃ and R₄ represent hydrogen and lower alkyl of 1 to 4 carbon atoms which may be the same or different, i.e., independently selected from methyl, ethyl, propyl, isopropyl, butyl, isobutyl, etc., and wherein m and n represent

positive integers the sum of which has a minimum average value of at least 7 so that the molecular weight of the accelerator is at least about 400.

The alkylene oxide adducts encompassed by the above formula may be prepared according to procedures well established in the art such as those described in United States Patents 1,970,578; 2,213,477; 2,575,832; 2,593,112 and 2,676,975. For example, a selected 1,4-butyne diol can be reacted with one or more alkylene oxides in the presence of a small amount of catalyst usually an alkaline catalyst such as sodium hydroxide at atmospheric or super-atmospheric pressure employing elevated temperatures ranging from e.g., about 100° to 200° C. The reaction can be conducted in the presence of an inert solvent and to the extent desired conventional heat transfer means can be employed to remove the heat of reaction.

The amount of alkylene oxide employed in the reaction will depend upon the average molecular weight of the product desired. To obtain such products, the 1,4-butyne diol is treated with the alkylene oxide until each hydroxyl hydrogen contains at least one mole of ethylene oxide in accordance with the above formula. The addition of the alkylene oxide to each hydroxyl group can be balanced or unbalanced, i.e., each may contain approximately the same or different average number of oxyalkylene groups per chain.

As above mentioned, the molecular weight of the polyoxyalkylenated 1,4-butyne diol depends upon the amount of ethylene oxide utilized in the reaction and can be readily determined by analysis of hydroxyl content. The hydroxyl number is a measure of and is proportional to the hydroxyl concentration per unit of weight. The hydroxyl number is defined in terms of milligrams of potassium hydroxide equivalent per gram of the 1,4-butyne diol reaction product, and is determined by reacting acetic anhydride (in pyridine solution) at refluxing temperature with the hydroxyl groups of the alkylene oxide-1,4-butyne diol reaction product. The unreacted anhydride and acetic acid formed are back-titrated with aqueous sodium hydroxide using phenolphthalein as an indicator. The molecular weight can be readily calculated from the hydroxyl number according to the following formula:

$$MW = \frac{\text{functionality} \times 1000 \times 56.1}{\text{Hydroxyl No.}}$$

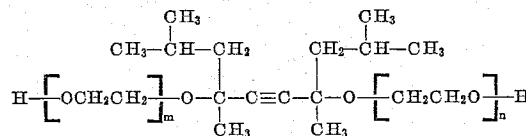
The amount of water-soluble polyoxyalkylenated 1,4-butyne diol employed in the developer composition is not especially critical and accordingly, may vary over a wide range. In this regard, it has been found that amounts ranging from as little as 0.25 grams up to 30 grams and higher per liter of developer composition are particularly beneficial. Proportions substantially in excess of the aforementioned would not ordinarily be warranted since the attendant improvement would, in many instances, be offset by the increased costs involved. Within the concentration ranges recommended, it is found that the above compounds provide speed increases on the order of 50% and higher than can be expected with the use of conventional developer compositions of the type currently available.

The polyoxyalkylenated butyne diols contemplated for use in accordance with the present invention must conform to two essential requirements namely, they must (1) be water soluble, and (2) contain a total of at least 7 combined alkylene oxide units. The question of water-solubility assumes considerable significance in connection with compounds encompassed by the above formula wherein one or more of the pendant R groups is alkyl. As will be readily apparent, as the number of carbons is increased, the compound becomes correspondingly more hydrophobic. However, within the limitation expressed in the above formula it is found that the desired degree of water-solubility is obtained regardless of the hydrophobicity introduced as a result of the pendant alkyl substituents, if the number of combined alkylene oxide units

is at least 7. For example, it is found that compounds containing less than the prescribed minimum of combined alkylene oxide units do not possess the requisite solubility in aqueous developer solutions and tend to yield an undesirable scum.

Expressed on a percentage basis, optimum realization of the results provided herein is obtained with compounds wherein the alkylene oxide units comprise at least 60% and more preferably from 75% to 95% of the butyne diol derivative. The amount of combined alkylene oxide units may exceed the aforesaid maximum since all of the derivatives within this range possess the requisite solubility in silver halide developer compositions. Expressed in terms of molecular weight, the polyoxyalkylenated 1,4-butyne diols contemplated for use herein fall within a range of from about 400 up to several thousand, i.e., on the order of 10-11,000. Particularly beneficial results are obtained however, with derivatives having molecular weights within the range of from about 900 to about 5,000. Thus, the sum of *m* and *n* in the above formula can have an average value ranging from about 7 to about 250 with a range of about 15 to about 100 being preferred. The higher molecular weight materials are obtained in the form of waxy, amorphous solids. However, no particular difficulty is encountered in forming aqueous solutions therewith since the combined alkylene oxide units are sufficient to provide the necessary water-solubility.

The improvements provided by the present invention are particularly manifest with the use of polyoxyethylated derivatives of 1,4-dimethyl-1,4-diisobutyl-1,4-butyne diol. These adducts can be represented according to the following structural formula:



wherein *m* and *n* have the meanings given above.

The materials encompassed by the above formula are available commercially from the Air Reduction Chemical and Carbide Company, a Division of Air Reduction Company, under the trade name Surfynol. Such products are identified according to a numerical code number which indicates the percentage of combined ethylene oxide units, e.g., Surfynol 485 and Surfynol 495 connote compounds of the above formula containing respectively, 85% and 95% combined ethylene oxide.

Without intending to be bound by any particular theory as to the action of the above compounds in the developing process, it has been postulated that there is involved an adsorption of the polyoxyalkylenated butyne diol material on the silver halide grains with the consequent formation of micelles. During the initial stages of development, the undissociated developing agent molecules are probably solubilized due to the effects of the lipophilic groups of the micelles. During the course of the development reaction and as the concentration of the developing agent decreases, fresh developing agent is supplied due to the effects of the lipophilic groups of the adsorbed micelles, thus solubilizing more developing agent.

However, many of the development accelerators heretofore provided and especially those having the desired softening or swelling effects, have nevertheless been found to otherwise deleteriously affect the gelatin emulsion. In many instances, such compounds undesirably affect the physical properties of the gelatin such as a lowering of the gelatin melting point and setting point. In contradistinction, there is little or no permanent swelling effect with the compounds of the present invention and upon removal of the emulsion from the developing solution and washing, the original physical properties of the gelatin are substantially restored. Moreover, the excel-

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lent water-solubility of the butyne diol derivatives of the present invention assures thorough and uniform distribution thereof throughout the emulsion which, of course, in the case of a multi-layer color element is of primary import in achieving good color balance.

The improvements provided by the present invention are not dependent upon the use of any particular type of silver halide developer. Accordingly, the latter may be of the hydroquinone type, i.e., those which contain hydroquinone, potassium metabisulfite and potassium bromide, or they may be of the metolhydroquinone type, i.e., those which contain p-methylaminophenol, sodium sulfite, sodium bisulfite, hydroquinone, sodium carbonate, and potassium bromide. Alternatively, the developer composition may be of the so-called borax type, i.e., those which contain p-methylaminophenol, sodium sulfite, hydroquinone, borax and potassium bromide. In short, the improvements provided by the present invention are readily obtained with practically all types of exposed silver halide emulsions.

The 1,4-butyne diol polyoxyalkylenated derivatives of the present invention find exceptional utility and provide particularly beneficial results when added to black and white developer compositions intended for use in connection with the reversal process of color photography. As is well known, the latter process involves the formation of color component images in each of a plurality of super-imposed light-sensitive silver halide emulsion layers each containing a non-diffusing color former by a first development of exposed silver halide whereby silver images only are formed, followed by re-exposure and a second development to form silver images and dye images in situ in the reverse image areas of the emulsion layers. Not only is there obtained an increase in the effective reversal speed of each of the dye images formed in the sensitized layers on the order of 50% and greater but, in addition, it is found that other advantageous results are obtained such as improved brightness, color saturation and color balance among the various layers.

The following examples are given for purposes of illustrating the present invention and are not to be regarded in any way as being limitative thereof.

EXAMPLE I

Amateur film having a gelatin-silver halide emulsion containing 2% silver iodide and 98% silver bromide was exposed to an image and treated for 5 minutes with a developer solution of the following formula:

	Grams
Metol	1.5
Sodium sulfite, anhydrous	45
Sodium bisulfite	1
Hydroquinone	3
Sodium carbonate, monohydrated	6
Potassium bromide	.8
Water to make 1 liter.	

The developed film is then fixed and washed in conventional manner.

A second sample of the same film is subjected to identical exposure. The exposed film is treated for 5 minutes with the above developer composition further provided with 4 cc. of polyoxyalkylenated 1,4-dimethyl-1,4-diisobutyl-1,4-butyne diol containing 75% combined ethylene oxide units. The relative speed obtained in the case of the conventional, i.e., unmodified developer, is 100 whereas the speed obtained with the butyne diol derivative-containing developer is 150. Moreover, the increase in speed did not entail any significant changes in clearness, gamma or D-Max.

The following examples illustrate the improved results obtained when the polyoxyalkylenated 1,4-butyne diol is added to a black and white developer employed in connection with the reversal process of color photography.

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EXAMPLE II

A multi-layer photographic film having three superimposed gelatin-silver halide emulsion layers sensitized respectively to the blue, green and red spectral regions, each containing respectively, a non-diffusing color former for yellow, magenta and cyan and having the blue sensitive layer outermost, was exposed to an image and developed for 9 minutes in a conventional black and white developer of the following composition:

	Grams
Metol	1.5
Sodium sulfite, anhydrous	45
Sodium bisulfite	1
Hydroquinone	3
Sodium carbonate, monohydrated	6
Potassium Bromide	.8
Water to make 1 liter.	

The film was then hardened for 3 minutes in a 30% aqueous solution of potassium chrome alum, washed for 3 minutes and given a reversal exposure for 1 minute at 1 foot distance from a No. 2 Photoflood lamp.

The so-exposed film was then immersed for 10 minutes in a conventional color developer solution of the following composition:

	Grams
Sodium hexametaphosphate	1
Sodium bisulfite	1
p-Aminodiethylaniline HCl	3
Sodium carbonate (monohydrate)	60
Hydroxylamine HCl	1
Potassium bromide	1.5
Water to make 1 liter.	

The developed film was short-stopped for 3 minutes in a bath of the following composition:

Sodium acetate	gms. 20
Acetic acid	cc. 10
Water to make 1 liter.	

The short-stopped film was hardened for 5 minutes in a 3% aqueous solution of potassium chrome alum.

After washing for 5 minutes in running water, the film was treated in a bleach bath of the following composition:

	Grams
Di-potassium mono-sodium ferricyanide	60
Potassium bromide	15
Disodium phosphate	13
Sodium bisulfate	6
Water to make 1 liter.	

The developed material was washed for 5 minutes and then fixed for 3 minutes in a solution of the following composition:

	Grams
Hypo	200
Borax	10
Water to make 1 liter.	

After fixing, the film was washed for 10 minutes in running water and allowed to dry.

A similar film treated in the identical manner but with 5 cc. of polyoxyethylenated 1,4-butyne diol of Example I added to the black and white developer and developed for only 3 minutes at the same temperature was compared with the film treated in the unmodified black and white developer. In each case, the dye densities obtained in each of the three sensitized layers was measured with red, green and blue light respectively. The results obtained indicated that the treatment with the modified black and white developer yielded an effective emulsion speed in each layer which was at least 0.30 log E greater than that obtained with the use of the unmodified black and white developer.

EXAMPLE III

Example II is repeated except that the amount of polyoxyethylenated 1,4-butyne diol included in the modified black and white developer is increased to 10 cc. In each case, the reversal image obtained in the three sensitized layers was measured and it was found that the effective increase in the speed in each such layer was at least 0.45 log E greater than that obtained with the film sample which had been treated with the unmodified black and white developer.

In each of the above examples, the noted improvement in film speed was obtained without any attendant adverse effects on the emulsion fog characteristic and/or the photographic quality of the image produced, i.e., clearness, contrast, and the like. The results of Example II are particularly significant. As indicated therein, marked improvement in film speed was obtained in the case of the modified black and white developer, as manifested by the density measurement results, despite the fact that the developing time was only one-third of that required in the case of the unmodified black and white solution.

As will thus be readily apparent, the use of developing compositions modified in accordance with the teachings of the present invention greatly accelerate the processing of photographic film to an extent heretofore unattainable. The commercial significance of such a process from an economic standpoint alone would be of considerable magnitude.

Results similar to those described in the above examples are obtained with the use of polyoxyalkylenated 1,4-butyne diols other than those specifically exemplified. As examples of such other compounds there may be mentioned in particular and without limitation the polyoxyethylenated and polyoxypropylenated derivatives of the following compounds:

- 1,4-butyne diol.
- 1,1,4,4-tetramethyl-1,4-butyne diol.
- 1-methyl-4-ethyl-1,4-butyne diol.
- 1,1-diisopropyl-3-ethyl-1,4-butyne diol, etc.

Moreover, similar improvement in emulsion speed is obtained when the foregoing examples are repeated but wherein the particular polyoxyethylenated 1,4-butyne diols contain, respectively, the following percentages of combined ethylene oxide: 60%, 70%, 85%, 90% and 95%. However, when the ethylene oxide content is reduced to a value substantially below 60%, e.g., 50-55% and lower, there is a pronounced tendency for the polyoxyethylenated derivative in question to "oil out" and form a scum-like deposit on the photographic film materials treated therewith.

This problem becomes increasingly manifest as the molecular weight of the 1,4-butyne diol component is increased, i.e., as the degree of alkylation is increased. Accordingly, within the limitations defined hereinbefore, it is found that maximum realization of the improvements provided by the present invention is promoted by correspondingly increasing the percentage of combined alkylene oxide units as the molecular weight of the butyne diol component is increased. Thus, in the case 1,4-butyne diol per se, i.e., unsubstituted, it is found that optimum results are obtained with polyoxyalkylenated derivatives thereof wherein the total number of combined alkylene oxide units has an average value within the lower portion of the range specified hereinbefore, e.g., from 7 to 12. Conversely, in the case of the higher alkylated butyne diol derivatives, e.g., polyoxyalkylenated 1,4-dimethyl-1,4-diisobutyl-1,4-butyne diol, particularly beneficial results are realized with alkylene oxide contents having an average value of at least about 15 and up to 30 and higher. Moreover, it will be understood that the polyoxyalkylenated 1,4-butyne diol derivatives may be effectively employed in the form of their mixtures, i.e., two or more derivatives containing different percentages of combined alkylene oxide. Furthermore, the improvements provided by the present invention are likewise obtained with the use of

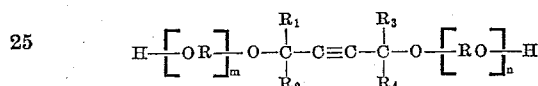
compounds which result from the reaction of a 1,4-butyne diol compound with mixtures of ethylene oxide and propylene oxide. Accordingly, such materials are to be regarded as equivalents to those more specifically described hereinabove.

It will also be understood that the specific developing agents described in the above examples may be replaced by other developing agents of the type more fully described above. In this regard, it should be recognized that any of the conventional silver halide developing agents are suitable for use herein and accordingly, this particular feature is in no sense a critical factor in the practice of the present invention.

This invention has been described with respect to certain preferred embodiments and there will become obvious to persons skilled in the art other variations, modifications and equivalents which are to be understood as coming within the scope of the present invention.

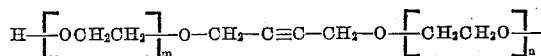
What is claimed is:

1. An aqueous developer solution containing a silver halide photographic developing agent and a small amount of a development accelerator comprising a water-soluble polyoxyalkylenated butyne-2-diol-1,4 of the formula:



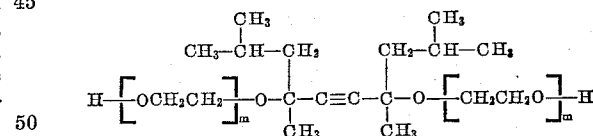
wherein R is selected from the group consisting of ethylene and propylene and R₁, R₂, R₃ and R₄ are independently selected from the group consisting of hydrogen and lower alkyl and wherein m and n represent positive integers the sum of which has a minimum average value of at least 7.

2. An aqueous developer composition according to claim 1 wherein said development accelerator comprises a compound of the formula:



wherein m and n represent positive integers the sum of which has an average value of 7 to 100.

3. An aqueous developer composition according to claim 1 wherein said developer accelerator comprises a compound of the formula:

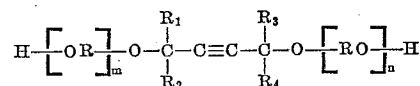


wherein m and n represent positive integers the sum of which has an average value of 7 to 100.

4. An aqueous developer composition according to claim 3 wherein said development accelerator is present in amounts ranging from 0.25 grams to 30 grams per liter of developer composition.

5. An aqueous developer composition according to claim 3 wherein said silver halide developing agent comprises hydroquinone.

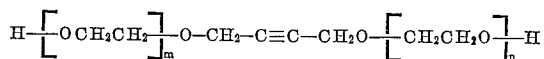
6. A process of developing a silver halide image which comprises treating an exposed silver halide emulsion with an aqueous developer composition containing a silver halide developing agent in the presence of a water-soluble polyoxyalkylenated butyne-2-diol-1,4 of the formula:



wherein R is selected from the group consisting of ethylene and propylene and R₁, R₂, R₃ and R₄ are independently selected from the group consisting of hydrogen and lower alkyl and wherein m and n represent positive integers the sum of which has a minimum average value of at least 7.

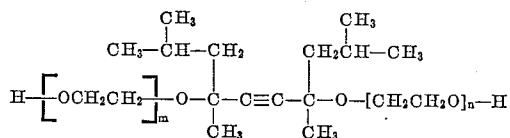
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7. A process according to claim 6 wherein said development accelerator comprises a compound of the formula:



wherein m and n represent positive integers the sum of which has an average value of 7 to 100.

8. A process according to claim 6 wherein said development accelerator comprises a compound of the formula:

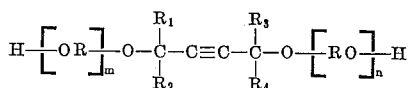


wherein m and n represent positive integers the sum of which has an average value of 7 to 100.

9. A reversal process of photography in which an exposed photographic element having at least one light-sensitive silver halide emulsion layer containing a non-diffusing color former is (a) given a first development in an aqueous alkaline developing solution containing a silver halide developing agent to form silver images only, (b) re-exposed to light, (c) given a second development in an aqueous developer solution containing a primary aromatic amino color developing agent to form both silver and dye images in the reverse areas of said emulsion layer; said process being characterized in that the first development is carried out in the presence of a development ac-

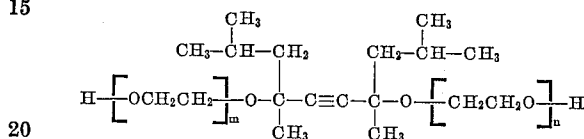
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celerator comprising water-soluble polyoxyalkylenated butyne-2-diol-1,4 of the formula:



wherein R is selected from the group consisting of ethylene and propylene and R_1 , R_2 , R_3 and R_4 are independently selected from the group consisting of hydrogen and lower alkyl and wherein m and n represent positive integers the sum of which has a minimum average of at least 7.

10. A process according to claim 9 wherein said first development is carried out in the presence of a development accelerator comprising a compound of the formula:



wherein m and n represent positive integers the sum of which has an average value of 7 to 100.

11. A process according to claim 9 wherein said silver halide developing agent comprises hydroquinone.

No references cited.

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Disclaimer

3,291,607.—*Fritz Dersch*, Binghamton, *Betty D. Fadden*, Johnson City, and *William L. Wike*, Endicott, N.Y. WATER-SOLUBLE POLYOXY-ALKYLENATED BUTYNE-2-DIOL-1,4 DEVELOPMENT ACCELERATORS. Patent dated Dec. 13, 1966. Disclaimer filed Sept. 30, 1982, by the assignee, *Eastman Kodak Co.*

Hereby enters this disclaimer to all claims of said patent.

[*Official Gazette March 22, 1983.*]