United States Patent Office

3,690,892
Patented Sept. 12, 1972

3,690,892

ELIMINATING PROCESSING DEFECTS IN LIGHT-SENSITIVE SILVER HALIDE MATERIALS

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No Drawing. Filed Apr. 6, 1970, Ser. No. 26,087
Int. Cl. G03c *1/02, 1/30*
U.S. Cl. 96—110 15 Claims

ABSTRACT OF THE DISCLOSURE

Incorporating a water-soluble inorganic acid salt (e.g., cadmium nitrate) and a water-soluble alkylenediamine polycarboxylic compound (e.g., disodium salt of ethylenediamine tetraacetic acid) into a light-sensitive silver halide emulsion layer or a contiguous layer eliminates undeveloped areas where development normally should have occurred caused by localized pre-wetting of the exposed photosensitive surface prior to immersing the photographic element in the first processing solution.

This invention relates to a method for reducing undesirable, undeveloped areas of developed photographic film or paper caused by localized pre-wetting of the exposed paper or film surface. More particularly, the invention relates to photographic emulsion layers or gelatin overcoats in photographic materials containing both a water-soluble inorganic acid salt of cadmium, cobalt, manganese, palladium or zinc, and a water-soluble alkylenediamine polycarboxylic compound.

Photographic silver halide emulsion layers are known to be enhanced by the presence of water-soluble inorganic acid salts of cadmium, cobalt, manganese, palladium or zinc in that they exert an initial antifog action on silver halide emulsions, especially on silver bromoiodide emulsions, and also have remarkably good antifoggant action during incubation of the coatings. (See U.S. Pat. 2,839,405 and U.S. Pat. 2,566,263.) This is true even with stabilized silver bromoiodide emulsions which have been sensitized with alkylene oxide polymers or other stabilizing materials.

While the presence of these water-soluble inorganic acid salts insures better keeping stability of the unexposed silver halide emulsion, a new problem is raised in the photographic element. This problem, which is the concern of our invention, occurs during processing of the said photographic material and is noticed as undeveloped areas where development should normally occur. This phenomenon is caused by localized pre-wetting of the exposed photosensitive surface, such as by touching it with wet fingers or by splashing with liquid, for instance, developer solution prior to immersing the photographic element in the first processing solution.

We have found that these defects observed in those emulsions containing polyvalent metal ions of the type mentioned above are eliminated when there is also present in the emulsion, or in a layer contiguous with the emulsion layer, ethylenediamine tetraacetic acid or an equivalent water-soluble alkylenediamine polycarboxylic compound, which is useful in photographic silver halide emulsions. Although ethylenediamine tetraacetic acid and some of its derivatives have been used in photography for other purposes (see, for instance, U.S. Pats. 2,666,700 and 3,458,316), to the best of our knowledge they have not been used for this purpose or in combination with the metals as claimed herein.

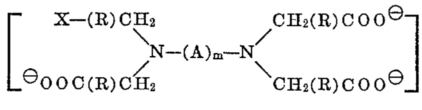
The effective amount of alkylenediamine polycarboxylic compound needed to prevent the described defects, is proportional to the level of the polyvalent metal ion present. When the metal salt is cadmium nitrate, a suitable range is 0.8 mole of disodium salt of ethylenediamine tetraacetic acid or a derivative of it per mole of cadmium nitrate to 0.01 mole of disodium salt of ethylenediamine tetraacetic acid or a derivative thereof per mole of cadmium nitrate. A preferred range is between about 0.45 and about 0.25 mole of disodium salt of ethylenediamine tetraacetic acid per mole of cadmium nitrate present. When the inorganic acid salt is of cobalt, manganese, palladium or zinc, and when the alkylenediamine polycarboxylic compound is an equivalent to it for use in photographic silver halide emulsions, the same ranges of mole proportions of materials are to be used as with the disodium salt of ethylenediamine tetraacetic acid and cadmium nitrate.

The inorganic salts are the water-soluble inorganic salts of cadmium, cobalt, manganese, palladium and zinc such as the chlorides, bromides, nitrates and sulfates. Examples of the compounds which can be employed are as follows: cadmium chloride, $CdCl_2$; cadmium nitrate, $Cd(NO_3)_2\cdot 4H_2O$; cobalt nitrate, $Co(NO_3)_2\cdot 6H_2O$; manganese chloride, $MnCl_2\cdot 4H_2O$; manganese sulfate, $MnSO_4\cdot H_2O$; palladium chloride, $PdCl_2$; palladium nitrate, $Pd(NO_3)_2$; palladium bromide, $PdBr_2$; zinc chloride, $ZnCl_2$; zinc nitrate, $Zn(NO_3)_2\cdot 6H_2O$; zinc sulfate, $ZnSO_4\cdot 7H_2O$, and the like.

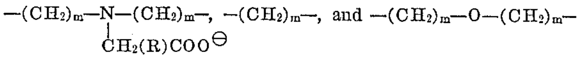
In the preparation of the silver halide emulsion, the metal, e.g., cadmium ion, can be introduced into the emulsion in the presence of a colloidal carrier as a water-soluble salt of cadmium, such as cadmium chloride or cadmium bromide mixed with the alkali bromide solution to which is added the silver nitrate solution to produce the formation of crystals or grains which consist primarily of silver bromide when an emulsion for use in a photographic element is intended. Except for the halide salts, a water-soluble cadmium salt, such as cadmium nitrate or acetate can be mixed with the silver nitrate solution which is then added to the alkali bromide solution during the emulsification step. The cadmium ion can also be introduced in the form of any other water-soluble salt which is not harmful to the photographic emulsion, such as cadmium iodide and cadmium sulfate.

The water-soluble inorganic acid salt can alternatively be incorporated in a layer which is over, under or otherwise contiguous with a light-sensitive silver halide emulsion layer.

Among the equivalent water-soluble alkylenediamine polycarboxylic compounds which are compatible with (i.e., not harmful to) the silver halide photographic emulsions to be employed in this invention are those compounds which can be depicted in part as an anion having the following general formula:



where each R is H or alkylene having 1 to 18 carbon atoms, preferably 1 to 5 carbon atoms, and can be the same or different, straight chain or branched; A is a divalent group chosen from



$$—(CH_2)_m—\underset{CH_2(R)COO^{\ominus}}{\underset{|}{N}}—(CH_2)_m—,\ —(CH_2)_m—,\ \text{and}\ —(CH_2)_m—O—(CH_2)_m—$$

X is H, cyano (CN), sulfonate ($SO_3^{\ominus}$), sulfate ($—OSO_3^{\ominus}$), sulfoxylate ($—SO_2^{\ominus}$) or carboxylate ($COO^{\ominus}$), and each *m* is a whole number from 1 to 5 and can be the same or different, and preferably is from 2 to 4. This anion is, of course, associated with water-soluble cations to form a compound, each cation of which can be the same or different, is compatible with (i.e., not harmful to) silver halide photographic emulsions, and is preferably an alkali metal (such as lithium, sodium, potassium or ammonium), but can also be hydrogen, or a cationic group yielding a soluble salt (such as from an amine, for instance, trialkylamines of 1 to 5 carbon atoms, such as diethylamine and trimethylamine, trialkanolamines of 1 to 5 carbon atoms, such as diethanolamine and triethanolamine, cyclohexylamine or an alkyl substituted ammonium hydroxide of 1 to 5 carbon atoms, such as tetraethyl- and tetramethyl-ammonium hydroxide, or from guanidine, diphenylguanidine, biguanidine, etc.).

While ethylenediamine tetraacetic acid, also known as tetracarboxyethylenediamine, referred to herein as "EDTA," or its alkali metal or ammonium salts, is the preferred material to be used, it is to be understood that equivalent water-soluble derivatives of EDTA, which are useful in silver halide photographic emulsions, can also be used.

Among the equivalent alkylenediamine polycarboxylic compounds which can be used are

ethylenediamine tetraacetic acid;
ethylenediamine tetraacetic acid, disodium salt;
ethylenediamine tetraacetic acid, tetrasodium salt;
1,5-pentylenediamine tetraacetic acid, dilithium salt;
1,5-pentylenediamine tetraacetic acid, mono(diethylamine)salt;
3-oxapentamethylenediamine tetraacetic acid;
bis{2-[di(carboxymethyl)amino]ethyl}ether;
bis{2-[di(carboxypentyl)amino]ethyl}ether;
bis{2-[di(carboxymethyl)amino]pentyl}ether;
bis{2-[di(carboxymethyl)amino]pentyl}ether, dipotassium salt;
bis{2-[di(carboxymethyl)amino]pentyl}ether, trimethylamine salt;
N,N-bis{2-[di(carboxymethyl)amino]ethyl}amino acetic acid;
N,N-bis{2-[di(carboxypentyl)amino]ethyl}amino acetic acid;
N,N-bis{2-[di(carboxymethyl)amino]pentyl}amino acetic acid;
ethylenediamine tetraacetic acid, ammonium salt;
ethylenediamine tetraacetic acid, monocyclohexylamine salt;
ethylenediamine tetraacetic acid, di(tetraethylammonium)salt;
ethylenediamine tetraacetic acid, tri(tetramethylammonium)salt;
ethylenediamine tetraacetic acid, tetra(triethylammonium)salt;
ethylenediamine tetraacetic acid, di(triethylamine)salt;
ethylenediamine tetraacetic acid, tetraguanidine salt;
ethylenediamine tetraacetic acid, mono(diphenylguanidine)salt;
ethylenediamine tetraacetic acid, tri(diphenylguanidine)salt;
ethylenediamine tetraacetic acid, mono(biguanidine)salt;
ethylenediamine tetraacetic acid, tetraguanidine salt;
ethylenediamine ethyltriacetic acid;
ethylenediamine cyano ethyl triacetic acid;
ethylenediamine ethyl sulfonate triacetic acid;
ethylenediamine ethyl sulfate triacetic acid;
ethylenediamine ethyl sulfoxylate triacetic acid;
ethylenediamine tetraacetic acid, mono(diethanolamine)salt;
ethylenediamine tetraacetic acid, tri(diethanolamine)-salt;
ethylenediamine tetrapropionic acid;
ethylenediamine tetraisobutyric acid;
ethylenediamine tetradodecanoic acid;
ethylenediamine tetrapentanoic acid;
ethylenediamine triaceticisohexanoic acid;
ethylenediamine tetraacetic acid, tetra(ethylenediamine)salt;

and the like. It is to be understood that photographically

useful equivalent materials to those illustrated herein are to be embraced as well.

Ethylenediamine tetraacetic acid is believed to associate in some way with the divalent metal ion, in a manner similar to the way a chelating agent behaves. It is preferred that this chelation takes place in the photosensitive emulsion layer. The two carboxy groups on one end of the alkylenediamine compound are believed to associate with a metal ion, such as cadmium, to tie it up or render it less mobile. When a penta or tetracarboxylic compound (like EDTA) is used, one molecule can potentially associate with more than one polyvalent metal ion at the same time and less moles are needed than when a tricarboxylic alkylenediamine compound is employed. Thus, while mole ratios of a penta or tetracarboxylic water-soluble alkylenediamine compound to metal salt which are less than one to one should be used, higher ratios reaching two to one can be employed with a tricarboxylic alkylenediamine compound. In general, however, an effective amount to substantially eliminate the undesired condition is all that is required and this can be as low as about 0.01 mole of water-soluble alkylenediamine compound per mole of divalent metal salt.

These compounds are normally introduced into the silver halide emulsion as photographic addenda, i.e. for example, after emulsion washing and preferably after the addition of the inorganic acid salt. The polycarboxymethylethylenediamine compounds are preferably added at the start or at the early part of the digestion stage of emulsion preparation when the emulsion is brought to maturation at relatively elevated temperatures and after undesirable salts have been removed by a washing operation.

The alkylenediamine polycarboxylic compound can alternatively be incorporated in a layer over, under or otherwise contiguous with a light-sensitive silver halide emulsion.

The alkylenediamine polycarboxylic compound and the water-soluble inorganic acid salt can both be incorporated in either the light-sensitive silver halide emulsion layer, or in a layer which is contiguous with the light-sensitive silver halide emulsion layer.

Although the invention is particularly useful in the preparation of negative type emulsions, the silver halide emulsions in which our invention can be adapted can comprise silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide or mixtures thereof. The emulsions can be coarse or fine grain and can be prepared by any of the well known procedures, e.g., single jet emulsions, double jet emulsions, such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al. U.S. Pat. 2,222,264; Illingsworth U.S. Pat. 3,320,069; and McBride U.S. Pat. 3,271,157. Surface image emulsions can be used or internal image emulsions such as those described in Davey et al. U.S. Pat. 2,592,250; Porter et al. U.S. Pat. 3,206,313; Berriman U.S. Pat. 3,367,778; and Bacon et al. U.S. Pat. 3,447,927. If desired, mixtures of surface and internal image emulsions can be used as described in Luckey et al. U.S. Pat. 2,996,382. Negative type emulsions can be used or direct positive emulsions such as those described in Leermakers U.S. Pat. 2,184,013; Kendall et al. U.S. Pat. 2,541,472; Berriman U.S. Pat. 3,367,778; Schouwenaars British Pat. 723,019; Illingsworth et al. French Pat. 1,520,821; Ives U.S. Pat. 2,563,785. The emulsions can be regular grain emulsions such as the type described in Klein and Moisar, J. Phot. Sci., vol. 12, No. 5, September/October, 1964 pp. 242–251.

The invention can also be used with emulsions which have been sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in Sheppard et al. U.S. Pat. 1,623,499; Waller et al. U.S.

Pat. 2,399,083; McVeigh U.S. Pat. 3,297,447; and Dunn U.S. Pat. 3,297,446.

The invention can also be used in those silver halide emulsions which contain speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these, as described in Piper U.S. Pat. 2,886,437; Dann et al. U.S. Pat. 3,046,134; Carroll et al. U.S. Pat. 2,944,900; and Goffe U.S. Pat. 3,294,540.

The silver halide emulsions used in the practice of this invention can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping. Suitable antifoggants and stabilizers each used alone or in combination include thiazolium salts described in Brooker et al. U.S. Pat. 2,131,038 and Allen et al. U.S. Pat. 2,694,716; the azaindenes described in Piper U.S. Pat. 2,886,437 and Heimbach et al. U.S. Pat. 2,444,605; the mercury salts as described in Allen et al. U.S. Pat. 2,728,663; the urazoles described in Anderson et al. U.S. Pat. 3,287,135; the sulfocatechols described in Kennard et al. U.S. Pat. 3,236,652; the oximes described in Carroll et al. British Pat. 623,448; nitron; nitroindazoles; the mercaptotetrazoles described in Kendall et al. U.S. Pat. 2,403,927; Kennard et al. U.S. Pat. 3,266,987 and Luckey et al. U.S. Pat. 3,397,987; the polyvalent metal salts described in Jones U.S. Pat. 2,839,405; the thiuronium salts described in Herz et al. U.S. Pat. 3,220,839; the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. 2,566,263 and Yutzy et al. U.S. Pat. 2,597,915.

The photographic elements of this invention can contain incorporated developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, ascorbic acid and its derivatives, reductones and phenylenediamines. Combinations of developing agents can be employed in the practice of the invention. The developing agents can be in a silver halide emulsion and/or in another suitable location in the photographic element. The developing agents can be added from suitable solvents or in the form of dispersions as described in Yackel U.S. Pat. 2,592,368 and Dunn et al. French Pat. 1,505,778.

The photographic emulsions and elements described in the practice of this invention can contain various colloids alone or in combination as vericles, binding agents and various layers. Suitable hydrophilic materials include both naturally occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water-soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

The described photographic emulsion layers and other layers of a photographic element employed in the practice of this invention can also contain alone or in combination with hydrophilic, water-permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in Nottorf .S. Pat. 3,142,568, issued July 28, 1964; White U.S. Pat. 3,193,386, issued July 6, 1965; Houck et al. U.S. Pat. 3,062,674, issued Nov. 6, 1962; Houck et al. U.S. Pat. 3,220,844, issued Nov. 30, 1965; Ream et al. U.S. Pat. 3,287,289, issued Nov. 22, 1966; and Dykstra U.S. Pat. 3,411,911, issued Nov. 19, 1968; particularly effective are those water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, those which have cross-linking sites which facilitate hardening or curing, those having recurring sulfobetaine units as described in Dykstra Canadian Pat. 774,054.

The photographic elements used with this invention can contain antistatic or conducting layers, such layers can comprise soluble salts, e.g., chlorides, nitrates, etc., evaporated metal layers, ionic polymers such as those described in Minsk U.S. Pat. 2,861,056 and Sterman et al. U.S. Pat. 3,206,312 or insoluble inorganic salts such as those described in Trevoy U.S. Pat. 3,428,451.

A preferred use of the invention is in photographic paper. A description of photographic paper is found in Kodak Photographic Papers, Professional Data Book G-1, 9th ed. (1967). A base material of these types would preferably be used in the present invention.

The photographic layers and other layers of a photographic element employed and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly (vinyl acetal) film, polystyrene film, poly(ethyene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically, a flexible support is employed, especially a paper support, which can be partially aceylated or coated with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

The photographic layers employed in the practice of this invention can contain plasticizers and lubricants such as polyalcohols, e.g., glycerin and diols of the type described in Milton et al. U.S. Pat. 2,960,404; fatty acids or esters such as those described in Robijns U.S. Pat. 2,588,765 and Duane U.S. Pat. 3,121,060; and silicone resins such as those described in Du Pont British Pat. 955,061.

The photographic layers employed in the practice of this invention can contain surfactants such as saponin; anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen U.S. Pat. 2,600,831; amphoteric compounds such as those described in Ben-Ezra U.S. Pat. 3,133,816; and water-soluble adducts of glycidol and an alkyl phenol such as those described in Olin Mathieson British Pat. 1,022,878.

The photographic elements employed in the practice of this invention can contain matting agents such as starch, titanium dioxide, zinc oxide, silica, polymeric beads including beads of the type described in Jelley et al. U.S. Pat. 2,992,101 and Lynn U.S. Pat. 2,701,245.

The photographic elements used in this invention can contain brightening agents including stilbenes, triazines, oxazoles and coumarin brightening agents. Water-soluble brightening agents can be used such as those described in Albers et al. German Pat. 972,067 and McFall et al. U.S. Pat. 2,933,390 or dispersions of brighteners can be used such as those described in Jansen German Pat. 1,150,274; Oetiker et al. U.S. Pat. 2,406,070; and Heidke French Pat. 1,530,244.

Spectral sensitizing dyes can be used conveniently to convert additional sensitivity to the light-sensitive silver halide emulsions of this invention. For instance, additional spectral sensitization can be obtained by treating the emulsion with a solution of a sensitizing dye in an organic solvent or the dye can be added in the form of a dispersion as described in Owens et al. British Pat. 1,154,781. For optimum results, the dye can either be added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes useful in sensitizing such emulsions are described, for example, in Brooker et al. U.S. Pat. 2,526,632, issued Oct. 24, 1950; Sprague U.S. Pat. 2,503,776, issued Apr. 11, 1950; Brooker et al. U.S. Pat. 2,493,748; and Taber et al. U.S. Pat. 3,384,486. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (tri or tetranuclear) merocyanines, complex (tri or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines (e.g., enamine hemicyanines), oxonals and hemioxonols.

Dyes of the cyanine classes can contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclein can contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and can be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano, or alkoxy groups. The dyes can be symmetrical or unsymmetrical and can contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain.

The meocyanine dyes can contain the basic nuclei mentioned above as well as acid nuclei such as thiohydantoins, rhodanines, oxazolidenediones, thiazolidenediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei can be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups or heterocyclic nuclei. Combinations of these dyes can be used, if desired. In addition, supersensitizing addenda which do not absorb visible light can be included, for instance, ascorbic acid derivaties, azaindenes, cadmium salts, and organic sulfonic acids as described in McFall et al. U.S.Pat. 2,933,390 and Jones et al. U.S. Pat. 2,937,089.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

A photographic chemically sensitized gelatino-silver chlorobromoiodide emulsion (62:37:1) containing suitable spreading and hardening agents is coated on a photographic paper support at 160 mg. silver/ft.². To the emulsion layer is added 7.4 mg./ft.² of hydroquinone as a development accelerator, 0.74 mg./ft.² of 1-phenyl-3-pyrazolidone as development accelerator and 168 mg. of cadmium nitrate/ft.² as an emulsion stabilizer. Over the emulsion layer is coated a protective gelatin layer at 100 mg. gelatin/ft.².

The above coated material is then uniformly flashed using available roomlight to ensure complete development, and machine processed in a conventional Elon hydroquinone developer, fixed, washed and dried. During processing, the print is deliberately immersed part way in the developer solution and held momentarily to produce a processing defect.

The processed print illustrates clear evidence of spot defects in the splashed developer areas and at the development surface developed surface line where the print was held during immersion in the developer.

EXAMPLE 2

A photographic material was prepared similar to that described in Example 1 except to the gelatin overcoat layer was added 22 mg./ft.² of the disodium salt of ethylenediamine tetraacetic acid. The emulsion layer contained 168 milligrams of cadmium nitrate as in Example 1.

No evidence of spot defects are visible when the above element is processed as described in Example 1.

While Example 2 illustrates the use of the sequestering agent in the gelatin overcoat layer, similar results are also obtained by placing the sequestering agent in the emulsion layer.

Other sequestering agents such as tetra sodium salt of EDTA and penta sodium salt of diethylene triamino pentaacetic acid show improvements towards preventing spot defects on the same order but in different degree as the disodium salt of EDTA as used in Example 2. These are illustrated in Examples 3 and 4.

EXAMPLE 3

A photographic material was prepared similar to that described in Example 1 except that to the gelatin overcoat layer was added 22 milligrams of the tetrasodium salt of ethylenediamine tetraacetic acid per ft.².

EXAMPLE 4

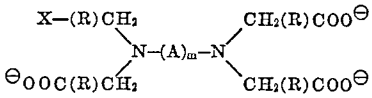
A photographic material was prepared similar to that described in Example 1 except that to the gelatin overcoat layer was added 18 milligrams of diethylene triamino pentaacetic acid per ft.².

Examples 3 and 4 showed no evidence of spot defects when processed as described in Example 1.

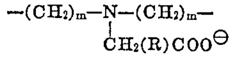
The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be undestood that variations and modifications can be effected within the spirit and scope of the invention.

What is claimed is:

1. A photographic element comprising a support, a silver halide emulsion layer and a water-permeable layer contiguous with said silver halide emulsion layer, at least one of said layers containing, in an effective amount to inhibit fog, a water-soluble inorganic acid salt of a metal selected from the group consisting of cadmium, cobalt, manganese, palladium and zinc and at least one of said layers containing a water-soluble alkylenediamine polycarboxylic compound which when ionized has the structure



wherein A is a divalent group selected from the group consisting of



$$-(CH_2)_m-\underset{\substack{|\\ CH_2(R)COO^{\ominus}}}{N}-(CH_2)_m-$$

$-(CH_2)_m-$ and $-(CH_2)_m-O-(CH_2)_m$

X is selected from the group consisting of hydrogen, cyano, sulfonate, sulfate, sulfoxylate and carboxylate; each R is independently selected from the group consisting of hydrogen and alkylene having 1 to 18 carbon carbon atoms; and each *m* is independently selected and is a whole number from 1 to 5; said alkylene diamine polycarboxylic compound being in an effective amount which when the element is exposed, spotted with developer and then developed by immersion in developer, reduces the occurrence of spots in the developed material.

2. The photographic element of claim **1** wherein said metal is cadmium.

3. The photographic element of claim **2** wherein said inorganic salt is cadmium nitrate.

4. The photographic element of claim **1** wherein said alkylenediamine polycarboxylic compound is the disodium salt of ethylenediamine tetraacetic acid.

5. The photographic element of claim **1** wherein said alkylenediamine polycarboxylic compound is the tetrasodium salt of ethylenediamine tetraacetic acid.

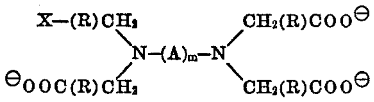
6. The photographic element of claim **1** wherein said alkylenediamine polycarboxylic compound is diethylene triaminopentaacetic acid.

7. The photographic element of claim **1** wherein said alkylenediamine polycarboxylic compound is in the silver halide emulsion layer.

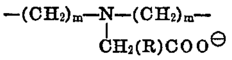
8. The photographic element of claim **1** wherein the alkylenediamine polycarboxylic compound is in a contiguous layer.

9. The photographic element of claim **1** wherein the said support is paper.

10. In a photographic element comprising a support, a light-sensitive silver halide emulsion layer and a water-permeable layer contiguous with said silver halide emulsion layer, at least one of said layers containing the water-soluble salt of an inorganic metal salt selected from the group consisting of cadmium, cobalt, manganese, palladium and zinc, the improvement which comprises incorporating a water-soluble alkylenediamine polycarboxylic compound into at least one of said layers in an effective amount which when the element is exposed, spotted with developer and then developed by immersion in developer, reduces the occurrence of spots in the developed material; said alkylenediamine polycarboxylic compound having when ionized by structure



wherein A is a divalent group selected from the group consisting of

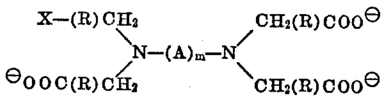


$-(CH_2)_m-\underset{\substack{|\\ CH_2(R)COO^{\ominus}}}{N}-(CH_2)_m-$

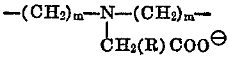
$-(CH_2)_m-$ and $-(CH_2)_m-O-(CH_2)_m-$

X is selected from the group consisting of hydrogen, cyano, sulfonate, sulfate, sulfoxylate nad carboxylate; each R is independently selected from the group consisting of hydrogen and alkylene having 1 to 18 carbon atoms; and each *m* is independently selected and is a whole number from 1 to 5.

11. A light-sensitive silver halide emulsion comprising silver halide and containing in an amount effective to inhibit fog a water-soluble inorganic acid salt of a metal selected from the group consisting of cadmium, cobalt, manganese, palladium and zinc, and containing a water-soluble alkylenediamine polycarboxylic compound in an effective amount which when the emulsion is exposed, spotted with developer and then developed by immersion in developer, reduces the occurrence of spots in the developed material; said alkylene diamine polycarboxylic compound having when ionized the structure



wherein A is a divalent group selected from the group consisting of



$-(CH_2)_m-\underset{\substack{|\\ CH_2(R)COO^{\ominus}}}{N}-(CH_2)_m-$

$-(CH_2)_m-$ and $-(CH_2)_m-O-(CH_2)_m-$

X is selected from the group consisting of hydrogen, cyano, sulfonate, sulfate, sulfoxylate and carboxylate; each R is independently selected from the group consisting of hydrogen and alkylene having 1 to 18 carbon atoms; and each *m* is independently selected and is a whole number from 1 to 5.

12. The emulsion of claim **11** wherein said inorganic metal is cadmium.

13. The emulsion of claim **11** wherein siad alkylenediamine polycarboxylic compound is the disodium salt of ethylenediamine tetraacetic acid.

14. The emulsion of claim **11** wherein said alkylenediamine polycarboxylic compound is the tetrasodium salt of ethylenediamine tetraacetic acid.

15. The emulsion of claim **11** wherein said alkylenediamine polycarboxylic compound is diethylene triaminopentaacetic acid.

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U.S. Cl. X.R.

96—94