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PHOTOGRAPHIC EMULSIONS CONTAINING NONPOLYMERIC AMINES

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ABSTRACT OF THE DISCLOSURE

Improved, novel photographic emulsions comprising a photosensitive silver halide and a synthetic peptizing hydrophilic colloid therefor, containing incorporated therein about one to 200 mole percent based on silver present therein of the acidic salt of a nonpolymeric amine of the group consisting of alkylamines, aromatic amines, alkaryl amines, cycloalkyl amines, and heterocyclic amines or mixtures thereof, said amines having one to 18 carbon atoms for each amino nitrogen atom contained therein. Also provided is a process for making the novel emulsions. 1,8-menthane diamine, a preferred nonpolymeric amine, also forms a useful complex with silver halide.

This application is a continuation-in-part of our earlier filed application, Ser. No. 542,448, now abandoned, filed Apr. 14, 1966.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to photographic products and more particularly to photographic emulsions and light-sensitive silver halide-containing media, and to a process for the preparation of gelatin-free photographic emulsions and the like.

(2) Description of the prior art

It is well known that natural gelatins are commonly employed as the protective colloid in photographic emulsions. These natural products are known to have serious disadvantages which have brought about a search for substitutes for gelatin which are synthetic, and, while retaining the requisite properties of gel formation and protective colloid action, would be free from the objectionable shortcomings.

Disadvantages of gelatin include variability in physical properties and chemical composition which lead to variations in the physical and photographic properties of the finished photographic emulsions. Gelatin products are brittle when dry and crack easily.

Attempts have been made to find a single synthetic material which would act as a protective colloid for precipitation of silver halide grains, and permit Ostwald ripening of these grains, which while being gelable, would allow chemical sensitization of the emulsion, and in addition would have good physical and mechanical properties in film form.

A number of materials have been developed which have the thermally reversible gelling properties of gelatin dispersions, and which can be used as gelling agents for photographic emulsions. However, although successful to a degree, the synthetic materials heretofore proposed have resulted in serious shortcomings when used in photographic emulsions, such as insufficient light-sensitivity, high fog levels, poor storability, etc.

The art has also attempted to find alternate methods for precipitating silver halide grains, so as to avoid the necessity for washing, etc. Thus quaternary ammonium or alkyl-substituted ammonium halides have been employed for this purpose with apparent success, as disclosed in U.S. Pats. 2,646,426 and 2,646,353. However, the necessity for rapid and essentially complete removal of the resulting ammonia or amine reaction products limits this approach. The pH used in these processes is maintained on the alkaline side, generally well above pH 7. It has therefore generally been considered necessary to avoid the presence of amines in photographic emulsions.

It is an object of this invention to provide improved gelatin-free photographic emulsions of superior light-sensitivity.

Another object of the invention is to provide light-sensitive photographic materials employing silver halide in which combinations of synthetic polymers are used, with amines or amine salts as a permanent part thereof, with improved results.

Other objects of the invention will be apparent from the disclosure hereinafter made.

It has been discovered that a variety of nonpolymeric amine halide salts have applicability as sources of halide ion for the formation of silver halide in synthetic photographic emulsion systems.

An extensive search of the chemical and patent literature reveals few instances where nonpolymeric amine halide salts have been used as sources of halide ion for photo emulsion preparations. However, in these cases, amines having a maximum of four carbon atoms were employed, the emulsion system was of alkaline pH, and rapid removal of all but a minor amount of the resulting ammonia or amine molecules via vaporization processes was necessary for useful emulsion preparation.

It has, therefore, generally been considered necessary to avoid the presence of substantial quantities of amines in photographic emulsions because of deleterious effects on photographic properties. It is known in the art that amines may be used to provide a sensitizing effect upon the silver halide grains, for example as taught in U.S. Pats. 2,521,925 (Lowe), 2,518,698 (Lowe), or 3,218,169 (Kelly), although the amounts of amines so employed are extremely minute, as is common procedure with other sensitizers commonly used in silver halide photographic emulsions. Amines or amine salts have also been used to affect the color of the developed silver image, i.e., as toner materials, as tought by Kendall, U.S. Pat. 2,512,721. Kendall teaches the use of 3-alkyl isoquinolines or mineral acid salts thereof in amounts of about 0.2% or less by weight of photographic emulsion to provide a toner effect on the developed image.

A process for the preparation of dispersions of silver halide grains in gelatin is described by Popeck, U.S. Pat. 3,241,970. Nitrogen-containing liquids are there employed as solvents for halide complexes of preformed silver halide and, after silver halide is reprecipitated, the nitrogen-containing solvent is removed by washing of the silver halide grains.

Thus, it is apparent from the prior art that amines have been employed as sensitizers in minute quantities. The art also teaches that amines, when used at basic pH or as salts, are completely removed from the photographic emulsions, either by volatilization or by thorough washing so as to render the final photoemulsion free of the amine compounds.

Thus, it is not obvious from the prior art that it is possible to employ amine compounds in significant quantities relative to silver halide as a permanent part of a photographic emulsion while retaining good photographic properties. Moreover, the prior art does not suggest that amine salts could be used as halide sources, under acidic

conditions, to produce photographic emulsions of superior quality.

The novel all-synthetic photographic emulsion systems of the present invention are prepared by treating non-polymeric amines with a hydrohalic acid or an organic halogen compound reactive toward amino nitrogen. The resulting amine halide salts are used as source of halide ion for the formation of silver halide by reaction with a soluble silver salt, e.g. silver nitrate. The pH of the systems is maintained below pH 7 during the formation of the silver halide grains.

To provide a protective colloid and gelable binder, a water-dispersible, film-forming polymeric material of the type heretofore found useful for photographic emulsions is employed to impart desired mechanical characteristics of the coated photographic emulsion system. Thus, useful binders for these purposes are polyvinyl alcohol, polyvinylpyrrolidone, polyacrylamides, gelatin, cellulose derivatives and the like. However, the more preferred binders are the systhetic binders such as polyvinyl alcohol, polyvinylpyrrolidone, polyacrylamides and polymethacrylamides and the like.

The method of the invention essentially comprises the step of precipitating silver halide grains by reacting a soluble silver salt in the presence of a synthetic peptizing hydropholic colloid for silver halide, at an acidic pH with a halide salt of an amine of the group consisting of alkylamines, aromatic amines, cycloalkylamines and heterocyclic amines, the said amines having from 1 to 18 carbon atoms for each nitrogen atom.

The amines employed in the practice of this invention are of widely varying structures, including primary, secondary and tertiary, or combinations thereof, involving aliphatic, cycloaliphatic, aromatic and heterocyclic systems. Illustrative amines include alkylamines, e.g. n-hexylamine, diethylamine, t-butylamine, triethylamine and the like, including diamines, such as ethylene diamine, 1-4-butane diamine and the like; and polyaminoalkanes, e.g. tetraethylenepentamine; 3,3'-diaminodipropylamine; methlyamine-bis-propylamine and the like; cycloalkylamines, e.g. cyclohexylamine, cyclohexylmethylamine, aminomethylcyclopentane, etc.; heterocyclic amines such as piperazine, morpholine, picoline and the like; aromatic and aralkyl amines such as aniline, p-phenylene diamine, benzylamine, etc. Mixtures of two or more amines can be employed if desired.

An amount of amine, as the acidic amine salt, is used which ranges from one to 200 mole percent based on the amount of silver ion present in the emulsion.

Salts of these amines are commonly employed in the preparation of the emulsion. These can be ordinary salts with halogen acids, e.g. hydrochloric, hydrobromic or hydroiodic acids, depending on the requirements of the emulsion as to silver halide species, or with non-halide, water-soluble acid. They can also be quaternary salts, as formed from certain amines with alkyl halides. Both of these types of salts are salts which acidic character such that the amine salt, in aqueous solution, gives a pH under 7.0; and they are generically referred to herein as "acidic salts" of the amines.

The emulsions prepared by the process of the invention can be ripened by the ripening or digesting steps known to the art for conventional emulsions. They are coated on suitable supports such as photographic grades or paper, or on film base or glass. When so coated, they can be exposed to light in the usual way and developed and fixed by conventional methods. When long-chain amines are used, or those which contain multiple aryl or heterocyclic radicals, they may confer a degree of water-repellency to the emulsion. In this case, addition of an amount of a lower alcohol or ketone, or other water-soluble organic solvent, to the developing solution may be useful.

All of the amine halide salts as described herein give silver halide emulsions, using synthetic polymeric binder systems, which when coated on a suitable supporting base, and exposed to light, form images upon exposure and normal development procedures.

A preferred amine is 1,8-menthane diamine, and preferred emulsions and photographic materials are those employing this compound or the complex of silver ion with this and similar compounds which are capable of forming such complexes. These photographic emulsions and materials yield negatives or prints having outstandingly good properties, with high contrast, high image density, low fog level and good light-sensitivity, even without added sensitizers or anti-fogging agents.

Without being bound by theory, it appears from calculations involving covalent radii, application of principles of bonding in silver-amine complexes and inspection of molecular models that intramolecular silver-amine complex formation is very likely in the case of 1,8-menthane diamine. The stereochemical conformation of the cyclohexane ring system of 1,8-menthane diamine allows such a nitrogen-silver-nitrogen complex to form without imparting undue strain on the molecule. A complex of silver halide and 1,8-menthane diamine can be prepared in the dark as a photosensitive material by reaction of the silver halide and the amine. Such a complex is a stable crystalline solid, having M.P. 137°–139° C.

From the results obtained in the process of the invention, it appears that the monomeric amine salts are simultaneously performing one or more of the following roles in the emulsion system herein disclosed: (a) halogen carrier, when amine halide salt is employed; (b) chemical sensitizer, where only very minute amounts are needed; and (c) complex formation, which has a possible restraining effect, thus reducing fog levels.

The presence of 1,8-menthane diamine in the photographic emulsions of the invention is particularly advantageous, resulting in high contrast and very low fog level in the exposed and developed materials.

It is possible also to form a different (non-hydrohalide) salt of the amine, incorporate this into the emulsion and add the halide ion as an inorganic salt, again maintaining the pH of the system below pH 7.

In another aspect of the process of the invention, a soluble, non-halide amine salt is added after normal formation of the silver halide dispersion. For example, after silver halide precipitation from silver nitrate and potassium halide in polyvinyl alcohol solution, the emulsion is made acidic by the addition of a few drops of nitric acid. To this acidic emulsion is added the nitrate salt of an amine, e.g. 1,8-menthane diamine. It has been discovered that as the amount of the added amine nitrate salt increases, a slight increase in sensitivity is observed, with a definite increase in contrast and decrease in fog level. When a sufficient amount of the nitrate salt has been added, prints are obtained having quality equal to those from an emulsion prepared using 1,8-menthane diamine dihydrobromide as the sole source of halide ion for silver halide.

The amino compounds employed are not removed from the emulsion, but are permitted to stay in the coating. The photographic materials thus prepared are nevertheless of good sensitivity and low fog, with excellent contrast.

As previously mentioned, a film-forming synthetic polymeric material is employed in conjunction with the silver halide in the emulsions prepared by the process of this invention. For example, polyvinyl alcohol may be used as a film-former, because of its water solubility, ease of crosslinking, permeability to photographic processing solutions, and the like. It is obvious that a variety of other water-dispersible, film-forming polymeric materials can be employed as the needs and requirements of these photographic systems are varied.

The emulsions prepared with amines according to the process of the invention can contain other materials known to be useful additives in conventional emulsions. These include sensitizers, anti-fogging agents (e.g. addi-

tional bromide), hardeners, stabilizers, coating aids and the like.

The following examples, in which all parts are by weight unless otherwise specified, will illustrate the best mode presently contemplated for practicing the invention.

EXAMPLE 1

The results obtained using various amine bromide salts are set forth in the following Table I, in which the amine and the amount used are shown. Other variables, such as pH, silver halide composition, amount and type of film-forming polymer, surfactant, hardening agent, emulsion preparation conditions and silver halide coating weight, are kept constant. It should be noted that no anti-fogging agents, sensitizers or other adjuvants are added.

The following procedure is employed in each case:

To a solution of 104 g. of 9.6 percent solution of polyvinyl alcohol (Elvanol 71–24) are added 10 ml. of constant boiling (48 percent) hydrobromic acid. While stirring the solution, the selected amine is added slowly to bring the pH of the solution to 3.1–3.2, pH being monitored constantly using an electric pH meter. Alternatively, the hydrobromide salt of the amine can be added. In the case of 1,8-menthane diamine, for example, 8.3 ml. of the amine were required to raise the pH of the solution to 3.20. Four ml. of 20 percent aqueous phosphoric acid solution are then added as a hardener for the polyvinyl alcohol.

The further steps in the process are carried out in the dark. Ten ml. of 5.9 N silver nitrate solution are added over a 60 second period while maintaining a stirring speed of 1000 r.p.m. The stirring is continued for 5 minutes more and a surfactant (4.0 ml. of 12 percent aqueous solution of Poly-Tergent J–300) is added during 30 seconds. After stirring for 3 minutes more, the emulsion is coated on baryta paper or specially prepared (subbed) plastic photographic film base. The coating is air dried, and the dried, coated material is stored in the dark.

TABLE I

Amine:	Amount of amine used
Ethylamine (70% in water) ml	7.9
Propylamine ml	7.8
n-Butylamine ml	9.2
t-Butylamine ml	10.1
t-Octylamine ml	14.7
Primene 81R [1] (long chain aliphatic amine with 14–16 carbon atoms) ml	20.8
Ethylenediamine ml	2.8
1,3-propylenediamine ml	3.6
1,4-butanediamine g	3.9
1,6-hexanediamine g	5.1
1,7-heptamethylenediamine g	6.0
1,8-octamethylenediamine g	6.4
1,9-nonamethylenediamine g	6.9
3,3'-diaminodipropylamine ml	4.2
Tetraethylenepentamine ml	4.15
Diethylamine ml	9.6
Dipropylamine ml	11.95
Dibutylamine ml	14.65
Hydroxyethylethylamine g	9.0
t-Butylaminoethanol g	10.25
1,4-cyclohexane-bis-methylamine ml	6.5
Triethylamine ml	14.7
Methylamino-bis-propylamine ml	4.5
t-Butylamine+ethylamine (1:1) ml	4.95+3.8
Tetraethyl ammonium bromide g	18.5
Tetrabutyl ammonium bromide g	28.4
Piperazine g	3.8
Morpholine ml	7.8
Bis(aminopropyl)piperazine ml	5.1
N-aminopropylmorpholine ml	8.8

TABLE I—Continued

Amine:	Amount of amine used
Pyridine ml	7.0
2-picoline ml	8.5
4-picoline ml	8.4
Quinoline [1] ml	10.9
Aniline ml	8.3
p-Phenylenediamine g	9.7
p-Aminobenzylamine g	5.4
1,8-menthane diamine ml	8.3
N,N,N',N'-tetramethyl-1,8-methane diamine ml	11.2

[1] Forms somewhat water-repellent emulsion. Developer contains 50% ethanol.

In the case where 1,8-menthane diamine was used, excellent prints of good contrast and low fog were made using 2 seconds exposure (31–35 foot candles, contact printer) and 110–120 seconds of development in a conventional metol-hydroquinone developer solution. An acid stop bath and the usual sodium thiosulfate fixing baths are used, followed by thorough washing.

Although not of the excellent quality attained when 1,8-menthane diamine is used, similar results are obtained when prints are made from paper coated with emulsions containing the other amines shown in the table. In some instances, lower contrast and the presence of fog were observed. These latter results can be improved by addition of small amounts of sensitizers, anti-foggants and stabilizers, as known in the art for use with conventional emulsions.

EXAMPLE 2

A series of emulsions are prepared employing aqueous polyvinyl alcohol, KBr and silver nitrate, and container 11.1 g. of silver bromide in 133 g. of emulsion. To these are added before coating 1,8-menthane diamine, neutralized with nitric acid to form the nitrate salt, as an aqueous about 50 percent solution, in amounts of 0, 5, 10, 25, 50 and 100 percent of the amount of menthane diamine used in Example 1.

After coating, drying, exposure to light and development, it was observed that as the amount of menthane diamine increased, there was a corresponding increase in contrast and image density and a decrease in fog. Accordingly, addition of as little as about 5 mol percent (based on the amount of silver present) shows an observable improvement in the photographic characteristics of the emulsions.

EXAMPLE 3

Formation of a complex of 1,8-menthane diamine with silver halide

To 40 g. of 1,8-menthane diamine contained in a flask provided with stirrer are added slowly, at room temperature, 2 g. of finely divided silver bromide (about 200 microns or less in size). The silver bromide powder becomes completely dispersed throughout the diamine, which is a liquid at room temperature. After a few minutes, a white precipitate begins to appear, whereupon stirring is stopped, and the mixture is permitted to stand at room temperature overnight. Thereafter, the white solid is removed from the excess amine by filtration, washed several times with diethyl ether and dried. The white amorphous powder thus obtained melted at 137°–139° C. Upon analysis, the following values were obtained:

Calculated for $C_{10}H_{22}N_2AgBr$ (percent): C, 33.54; H, 6.19; N, 7.82; Br, 22.31. Found (percent): C, 33.0; H, 6.1; N, 7.44; Br, 23.6.

When the silver-1,8-menthane diamine complex is prepared in the dark, from photosensitive silver bromide, a photosensitive material is obtained Thus, when 2 g. of very finely divided silver bromide, made in the dark by mixing equimolar amounts of silver nitrate and potassium bromide solutions, while stirring at high speed,

filtering, washing and drying, are added to 10 ml. of 1,8-menthane diamine, also stirring at high speed for several minutes, then permitting the mixture to stand at room temperature for two days, also in the dark, a white precipitate is obtained as above. A small amount of unreacted silver bromide is found to have formed a hard lump adhered to the bottom of the flask, from which the complex is easily removed by slurrying with ether, filtering, further washing with ether and drying.

About 1 g. of the silver bromide-1,8-menthane diamine complex thus prepared in the dark was added, in darkness and with stirring, to about 10 g. of 10 percent polyvinyl alcohol solution, and the dispersion was coated on baryta paper. The dried coating, after exposure to light in a contact printer and developing in the usual way with a metol-hydroquinone developer solution, formed a photographic image of good contrast and with little or no fog.

A visible image was formed when the coated paper was exposed to ultraviolet light for a sufficient length of time, without development.

In the same way as described above, complexes of 1,8-menthane diamine and silver iodide, and silver chloride, are made. These, likewise, are photosensitive when prepared in the dark.

What is claimed is:

1. A photographic emulsion comprising a photosensitive silver halide and a synthetic peptizing hydrophilic colloid therefor, containing incorporated therein about one to 200 mole percent based on silver present therein of the acidic salt of a nonpolymeric amine of the group consisting of alkylamines, aromatic amines, alkaryl amines, cycloalkyl amines, and heterocyclic amines or mixtures thereof, said amines having one to 18 carbon atoms for each amino nitrogn atom contained therein.

2. The photographic emulsion in accordance with claim 1, wherein said amine is 1,8-menthane diamine.

3. A photosensitive silver halide compound comprising the complex of silver halide with 1,8-menthane diamine.

4. A photosensitive silver halide coating containing 1,8-menthane diamine or salts thereof.

5. In the method for preparing photographic emulsions containing photosensitive silver halide grains, the step which comprises precipitating silver halide grains by reacting a soluble silver salt in the presence of a synthetic peptizing hydrophilic binder under acidic conditions with a halide salt of a nonpolymeric amine of the group consisting of alkyl amines, aromatic amines, alkaryl amines, cycloalkyl amines, and heterocyclic amines, said amines having 1 to 18 carbon atoms for each amino nitrogen atom contained therein, said halide salt being present in amount at least sufficient to form the principal source of halide ion for the precipitation of silver halide, which ranges from 1 to 200 mole percent of amine halide salt based on the amount of silver ion present in said emulsion.

6. The method of claim 5, wherein said nonpolymeric amine comprises 1,8-menthane diamine.

7. A method for preparing a photosensitive complex which comprises the step of reacting silver halide with 1,8-menthane diamine.

8. An ultraviolet sensitive photographic element comprising a support sheet and a complex of silver halide with 1,8-menthane diamine thereon.

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