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PHOTOGRAPHIC EMULSIONS CONTAINING AN ANTIFOGGANT AND ANTIPLUMMING AGENT

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This invention relates to light-sensitive silver halide emulsions and to such emulsions containing a particular fog inhibiting agent and a particular antiplumming agent.

It is well known that photographic emulsions on storage tend to lose sensitivity and to become spontaneously developable without exposure to light. There is normally a detectable amount of the silver salt reduced during development in the areas where no exposure was given. This is commonly called "fog," and sometimes called "chemical fog" where it is necessary to distinguish between it and the effects of accidental exposure to radiation; in this invention, I am not concerned with the latter.

Fog depends both on the emulsion and the conditions of development; for a given emulsion it increases with the degree of development. With constant development conditions, it tends to increase with time, temperature and relative humidity of storage conditions; it is common practice to make accelerated tests of the stability of photographic emulsions by storage at increased temperature or humidity, or both. It is, of course, desirable to have emulsions as stable as possible under the conditions of high temperature and humidity which may occur in tropical climates, for example. Fog usually appears over the whole area of the sensitive coating, but when severe, it frequently is non-uniform. Fog may also be caused by exposure to chemicals, for example, hydrogen sulfide and other reactive sulfur compounds, hydrogen peroxide, vapor, and strongly reducing materials. While antifoggants and stabilizers may protect, to some extent, against such effects, it is normally understood that an anti-foggant protects against spontaneous growth of fog during prolonged storage or storage at high temperatures and humidities, or during development to maximum contrast and speed, or both.

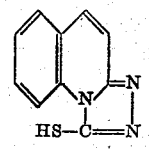
Silver halide emulsions, especially those used on paper supports, are often subject, on processing and especially on glazing, to that form of image degradation known as plumming. Compounds which reduce this effect are called "anti-plumming agents."

It is, therefore, an object of my invention to provide photographic silver halide emulsions stabilized against the formation of fog. Another object is to provide photographic silver halide emulsions which give rise to prints which can be hot glazed or ferrotyped without objectionable plumming. Still another object is to provide photographic silver halide emulsions having improved sensitivity without objectionable increase in fog when said emulsions are stored under adverse conditions of temperature and humidity. Other objects will become apparent from a consideration of the following description and examples.

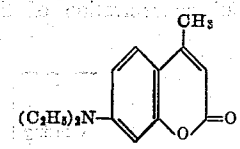
According to the present invention, I provide a light-sensitive silver halide emulsion containing 1':2'-dihydroquinolino-1':2':4:5-triazole(1:2:4)-3-thiol, or its water-soluble salts and 4-methyl-7-diethylaminocoumarin. Typical water-soluble salts of the above triazole compound which can be employed in my invention, include

alkali metal salts, such as sodium, potassium, etc., the ammonium salt, or substituted ammonium (e.g., triethylammonium, triethanolammonium, pyridinium, etc.) salts.

The above triazole compound which can be used in practicing my invention can be represented by the following formula:



The coumarin compound which can be employed in practicing my invention can advantageously be represented by the following formula:



In Williams U.S. application Serial No. 655,472, filed April 29, 1957, now U. S. Patent 2,887,378, issued May 19, 1959, there is described a method of stabilizing photographic silver halide emulsions and at the same time preventing plumming during the hot-glazing of photographic prints. This method comprises adding certain complex triazole compounds to the photographic emulsions during the preparation thereof. Among the triazole compounds described in Serial No. 655,472 is the particular triazole compound represented above. However, when sufficient triazole compound is added to prevent fogging of the photographic emulsions, it has been found that there is a certain speed loss resulting from the partial desorption of the spectral sensitizing dyes customarily employed in sensitizing photographic emulsions. It has been found that the above coumarin compound can be advantageously employed in combination with the triazole compound to obtain both the desired antifoggant effect and antiplumming effect. According to my method, the triazole compound can be employed in a concentration to give only the desired antiplumming effect and sufficient coumarin compound added to give the desired antifoggant effect. Under these conditions, I have found that little or no desorption of sensitizing dyes occurs. It is interesting to note that the coumarin compound employed in my invention has been found to have little or no antifoggant activity when employed alone in high-speed photographic silver halide emulsions. The effect obtained in my invention is somewhat similar to a synergistic effect of the type sometimes encountered in catalytic reactions.

It is interesting to note that other coumarin compounds, such as β-methylumbelliferone and 4-methyl-7-aminocoumarin, have been tried in combination with the triazole compound of my invention, but the useful effect illustrated below has not been obtained. On the other hand, the use of conventional antifoggant compounds, such as 5-methylbenzotriazole and 1-phenyl-5-mercaptotetrazole, does not provide effects comparable to the triazole compound used in my invention.

The preparation of silver halide emulsions involves three separate operations: (1) the emulsification and digestion of ripening of the silver halide, (2) the freeing of the emulsion from excess soluble salts, usually by washing, and (3) the second digestion or after-ripening to obtain increased sensitivity. (Mees, "The Theory of the Photographic Process" (1942).) I prefer to add the stabilizing agents after the final digestion or after-ripening, although they can advantageously be added prior to digestion.

The photographic emulsions used in practicing my in-

vention are generally of the developing-out type; also, it is to be understood that photographic emulsions of varying silver halide content can advantageously be used. The particular combinations used in my invention have been found particularly useful when employed in conjunction with gelatino-silver-chloride emulsions, although they can advantageously be employed for treating other silver halide emulsions, such as gelatino-silver-chlorobromide, bromide, chlorobromiodide, etc.

The compounds of my invention can advantageously be added to the emulsions in the form of their aqueous solutions or as solutions in a water-miscible organic solvent such as acetone, etc. The combinations should be uniformly mixed with the emulsions in order to assure uniform results in the finished emulsions. If desired, the compounds can be added before the final step of "after-ripening," or they can be added to the emulsions immediately prior to coating, as indicated above.

The most useful concentration of the triazole and coumarin compounds can be varied, depending upon the particular silver halide being treated, the presence or absence of other emulsion addenda, etc. The most useful concentration for a particular emulsion can be determined by adding a small amount, such as 1–2 grams per mole of silver halide, to the emulsion and then adding varying amounts of the other ingredients to separate portions of the same emulsion. The emulsions can then be coated, exposed in a sensitometer and then glazed to provide prints. The maximum density and fog in each of the prints can then be measured. In general, I have found that from about 0.1 to 1.0 gram per mole of silver (or silver halide) of the triazole compound is quite useful. In like manner, I have found that from about 2.0 to 6.0 grams per mole of silver (or silver halide) of the coumarin compound is sufficient to provide the unique effects illustrated in the following examples. In general, it has been found that the concentration of the triazole compound should be about 5 to 10 times the concentration of the coumarin compound in order to obtain the most beneficial effects, i.e., with a minimum amount of fog and a maximum density.

The following examples will serve to illustrate the unique effect of the triazole compound and the coumarin compound of my invention when employed simultaneously in an ordinary photographic silver chloride emulsion. The emulsion was divided into several batches and the separate batches treated with the addenda, identified in the following table; the concentration of the addenda being given in the parentheses following the chemical name. The emulsions were then exposed in the usual manner in a sensitometer and separate sections of each coating were developed for 2, 15 and 30 minutes as indicated in the table. The fog developed by each of these processes is shown. The relative speed, based on untreated emulsion and relative contrast for each of the coatings is also shown. The maximum density for each of the coatings, after glazing at 80° C. is also indicated.

In the following table there is also shown the effect produced by a conventional antifoggant, 5-methylbenzotriazole, when employed in combination with the coumarin compound of my invention. It is quite apparent that coating (*e*) is markedly superior to the other coatings shown in the table. The fog was at a minimum, while the maximum density was materially increased.

The developer used to treat each of the coatings had the following composition:

	Grams
N-methyl-p-aminophenol sulfate	1.7
Hydroquinone	7.0
Sodium sulfite, anhydrous	25.0
Sodium carbonate, anhydrous	35.0
Potassium bromide	0.45
Water to make 1 liter.	

The results obtained by processing the above emulsions are given in the following table. In the table, the sensitometric data were obtained from the coatings which were developed for 2 minutes.

Table

Coating	Addenda (g./mol. Ag)	Fog-Devel. Time			Sensitometric Data		
		2′	15′	30′	D max.	Rel. Speed	Rel. Contrast
(*a*)	None	.04	.20	.40	1.54	100	100
(*b*)	1′:2′-dihydroquinolino-1′:2′:4:5-triazole-(1:2:4)-3-thiol (1.5).	.10	.16	.20	1.72	90	110
(*c*)	4-methyl-7-diethylaminocoumarin (4.0)	.12	.15	.20	1.62	90	100
(*d*)	4-methyl-7-diethylaminocoumarin (8.0)	.12	.15	.20	1.66	90	100
(*e*)	1′:2′-dihydroquinolino-1′:2′:4:5-triazole-(1:2:4)-3-thiol (0.4) plus 4-methyl-7-diethylaminocoumarin (4.0).	.02	.04	.06	1.82	90	110
(*f*)	5-methylbenzotriazole (8.0)	.02	.12	.18	1.58	90	120
(*g*)	5-methylbenzotriazole (8.0) plus 4-methyl-7-diethylaminocoumarin (4.0).	.04	.08	.11	1.60	90	120
(*h*)	1′:2′-dihydroquinolino-1′:2′:4:5-triazole-(1:2:4)-3-thiol (0.4) plus 5-methylbenzotriazole (8.0).	.02	.06	.10	1.68	90	110

Instead of adding the triazole and coumarin compounds directly to the photographic emulsions, it is sometimes desirable to incorporate them in a separate colloid layer which is placed in contact with the silver halide emulsion layer. Under such conditions, of course, it is advisable to use a higher concentration of these compounds than indicated above.

The compounds of my invention function either in acid or alkaline photographic silver halide emulsions. In alkaline emulsions, water-soluble salts of the mercaptotriazole compound are formed to some extent, although it is to be understood that the salts of this compound can be used directly in photographic silver halide emulsions. Alkali metal salts of this mercaptotriazole can be formed by simply contacting such mercapto compound with an aqueous solution of an alkali metal hydroxide, such as sodium hydroxide, potassium hydroxide, etc. The ammonium salts of the mercapto compound can be prepared by simply contacting said mercapto compound with ammonia or an organic amine, such as pyridine, triethylamine, triethanolamine, aniline, etc.

The emulsions can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U.S. Patents 1,574,944, issued March 2, 1926, and 1,623,499, issued April 5, 1927, and Sheppard and Brigham U.S. Patent 2,410,689, issued November 5, 1946.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium, and platinum. Representative compounds are ammonium chloropalladate, potassium chloroplatinate, and sodium chloropalladite, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, issued August 31, 1948, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245, issued August 28, 1951, and 2,566,263, isssued August 28, 1951.

The emulsions can also be chemically sensitized with gold salts as described in Waller and Dodd U.S. Patent 2,399,083, issued April 23, 1946, or stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856, issued May 27, 1952, and Yutzy and Leermakers U.S. Patent 2,597,915, issued May 27, 1952. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-aurosulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850, issued November 15, 1949), polyamines, such as diethylene triamine (Lowe and Jones U.S. Patent 2,518,698, issued August 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925, issued September 12, 1950), or bis(β-aminoethyl)sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926, issued September 12, 1950).

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301, issued February 23, 1932; 1,846,302, issued February 23, 1932; and 1,942,854, issued January 9, 1934; White U.S. Patent 1,990,507, issued February 12, 1935; Brooker and White U.S. Patents 2,112,140, issued March 22, 1938; 2,165,338, issued July 11, 1939; 2,493,747, issued January 10, 1950; and 2,739,964, issued March 27, 1956; Brooker and Keyes U.S. Patent 2,493,748, issued January 10, 1950; Sprague U.S. Patents 2,503,776, issued April 11, 1950, and 2,519,001, issued August 15, 1950; Heseltine and Brooker U.S. Patent 2,666,761, issued January 19, 1954; Heseltine U.S. Patent 2,734,900, issued February 14, 1956; Van Lare U.S. Patent 2,739,149, issued March 20, 1956; and Kodak Limited British Patent 450,958, accepted July 15, 1936.

The emulsions may also contain speed-increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623, issued February 3, 1942; Carroll and Allen U.S. Patent 2,288,226, issued June 13, 1942; and Carroll and Spence U.S. Patent 2,334,864, issued November 23, 1943; and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162, issued May 10, 1955.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there may be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound. Some colloids which may be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19–26%; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide having a combined acrylamide content of 30–60% and a specific viscosity of 0.25–1.5 on an imidized polyacrylamide of like acrylamide content and viscosity as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing cyano-acetyl groups such as vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh and Smith U.S. Patent 2,768,154, issued October 23, 1956; or a urethane carboxylic acid compound of the type described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued October 1, 1957.

If desired, compatible mixtures of two or more of these colloids may be employed for dispersing the silver halide in its preparation.

The silver halide emulsions of my invention can be coated on any of the conventional, flexible photographic supports, such as paper, polyvinyl resin film, polyester film, etc. However, the emulsions of my invention are particularly useful in preparing photographic prints, in which case paper would ordinarily be used as the support. Other fibrous supports than paper can also be employed.

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.

What I claim as my invention and desired secured by Letters Patent of the United States is:

1. A photographic silver halide emulsion containing 4-methyl-7-diethylaminocoumarin and a compound selected from the group consisting of 1′:2′-dihydroquinolino-1′:2′:4:5-triazole-(1:2:4)-3-thiol and a water-soluble salt of 1′:2′-dihydroquinolino-1′:2′:4:5-triazole(1:2:4)-3-thiol.

2. A photographic silver chloride emulsion containing 4-methyl-7-diethylaminocoumarin and a compound selected from the group consisting of 1′:2′-dihydroquinolino-1′:2′:4:5-triazole-(1:2:4)-3-thiol and a water-soluble salt of 1′:2′-dihydroquinolino-1′:2′:4:5-triazole(1:2:4)-3-thiol.

3. A photographic gelatino-silver-chloride developing-out emulsion containing a stabilizing amount of 4-methyl-7-diethylaminocoumarin and sufficient compound selected from the group consisting of 1′:2′:-dihydroquinolino-1′:2′:4:5-triazole-(1:2:4)-3-thiol and a water-soluble salt of 1′:2′ - dihydroquinolino - 1′:2′:4:5 - triazole(1:2:4)-3-thiol, to prevent plumming of said photographic emulsion.

4. A photographic element comprising a support and a photographic silver halide emulsion containing 4-methyl-7-diethylaminocoumarin and a compound selected from the group consisting of 1′:2′-dihydroquinolino-1′:2′:4:5-triazole(1:2:4)-3-thiol and a water-soluble salt of 1′:2′-dihydroquinolino-1′:2′:4:5-triazole(1:2:4)-3-thiol.

References Cited in the file of this patent

UNITED STATES PATENTS

2,649,375	Davis	Aug. 18, 1953
2,887,378	Williams	May 19, 1959