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3,447,926

COLOR PHOTOGRAPHIC SILVER HALIDE ELEMENTS CONTAINING 4-SUBSTITUTED URAZOLES AND/OR CYCLOALKANE-1,3-DIONES

Clark Beckett and Everett H. Poppink, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey
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8 Claims

ABSTRACT OF THE DISCLOSURE

Multicolor photographic elements containing at least one camera speed spectrally-sensitized emulsion containing a carbocyclic-1,3-dione, preferably in combination with a 4-substituted urazole have greatly reduced tendency to undergo latent image changes during storage between image exposure and photographic processing.

This invention relates to photographic elements and more particularly to certain multicolor, multilayer photographic elements containing latent image stabilizers.

Multilayer color films normally contain separate emulsion layers which record separate regions of the spectrum, usually blue, green, and red. During development, yellow, magenta, and cyan dyes are formed in these layers respectively. Color negative camera films are frequently exposed and then held for considerable lengths of time before processing. This situation frequently arises with amateur color roll films when a customer may take pictures on a single roll of film over a period of several months before he has the roll processed. Since optimum color quality is obtained only when the separate emulsion layers are balanced for sensitivity and contrast, it is desirable that the latent images produced by exposure do not change during an extended hold before processing. Unless the latent image in each layer changes at the same rate and in the same direction, distortion of the color balance will occur.

It is known that storage of photographic materials, especially at elevated temperatures and humidities, will over a period of time tend to make unexposed silver halide developable during the photographic developing process resulting in unwanted silver development and in the case of color material unwanted dye often referred to as color fog. High speed emulsions such as are used in multicolor films are particularly subject to the formation of color fog when stored under undesirable conditions.

It is therefore an object of our invention to provide new multicolor photographic elements having spectrally-sensitized camera speed silver halide emulsions which have a greatly reduced tendency to undergo latent image changes during storage.

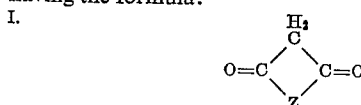
Another object is to provide novel multicolor photographic elements having silver halide emulsions that have a greatly reduced tendency to undergo latent image changes and a greatly reduced tendency to become fogged during long periods of storage.

Still other objects will become obvious from the following specification and claims.

These and other objects are accomplished with multicolor, multilayer photographic elements containing at least one camera speed spectrally-sensitized silver halide emulsion containing a carbocyclic 1,3-dione. A 4-substituted urazole can be used in combination with the cycloalkane-1,3-dione.

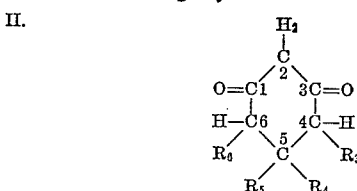
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Typical suitable carbocyclic 1,3-diones include those having the formula:



wherein Z represents the atoms required to complete a carbocyclic ring, e.g., having 5 to 6 carbons in the nucleus as cyclopentane, cyclohexane, cyclopentene, cyclohexene, etc., such that the said ring may be unsubstituted or substituted with groups, such as an alkyl (e.g., methyl, ethyl, butyl, hexyl, etc.); an aryl, (e.g., phenyl tolyl, methoxyphenyl, hexadecyloxyphenyl, naphthyl etc.); cyano; a carbalkoxy (e.g. carbomethoxy, carboethoxy, carbobutoxy, etc.), etc.

The preferred carbocyclic 1,3-diones include compounds shown to advantage by formula:



wherein R_3 and R_6 each represent a group selected from the class consisting of hydrogen; an alkyl (e.g., methyl, ethyl, butyl, etc.); an aryl (e.g., phenyl, tolyl, naphthyl, etc.); cyano; a carbalkoxy (e.g., carbomethoxy, carboethoxy, etc.); and R_4 and R_5 are each selected from the class consisting of hydrogen, an alkyl (e.g., methyl, ethyl, butyl, amyl, etc.); an aryl (e.g., phenyl, methoxyphenyl, ethoxyphenyl, hexadecyloxyphenyl, tolyl, naphthyl, etc.).

Typical examples of compounds included in Formula I that are used to advantage according to our invention are:

- (1) 5,5-dimethylcyclohexane-1,3-dione
- (2) 5-phenylcyclohexane-1,3-dione
- (3) 5-(p-methoxyphenyl)cyclohexane-1,3-dione
- (4) 4-cyano-5-phenylcyclohexane-1,3-dione
- (5) 5-(o-decyloxyphenyl) cyclohexane-1,3-dione
- (6) 5-(o-hexadecyloxyphenyl)cyclohexane-1,3-dione
- (7) cyclohexane-1,3-dione
- (8) 4,6-dicarbethoxy-5-methylcyclohexane-1,3-dione
- (9) 4,6-dimethyl-5-phenylcyclohexane-1,3-dione
- (10) 4,6-dicyano-5,5-dimethylcyclohexane-1,3-dione
- (11) 4-phenyl-5,5-diethylcyclohexane-1,3-dione
- (12) 5-methyl-5-phenylcyclohexane-1,3-dione
- (13) cyclopentene-1,3-dione
- (14) 4,4-dimethylcyclopentane-1,3-dione

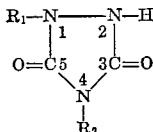
These and other compounds of Formula I are used to advantage according to our invention.

The cyclohexane-1,3-diones are prepared by the condensation of α,β -unsaturated ketones with malonic acid esters, cyano acetic acid esters, or aryl acetic acid esters in the presence of basic catalysts such as sodium ethoxide. The resulting compounds which contain carbalkoxy groups can be readily hydrolyzed to the corresponding carboxy compounds and decarboxylated. The starting α,β -unsaturated ketones are prepared by condensation of ketones with aldehydes and ketones. The preparation of 5,5-dimethylcyclohexane-1,3-dione may be given as an example of the preparation of a typical cyclic 1,3-diketone. The preparation involves the condensation of mesityl oxide with diethyl malonate in the presence of sodium ethoxide. This is followed by hydrolysis of the ester group present in the resulting intermediate and decarboxylation. A number of

the cyclopentane-1,3-diones are described in the literature as for example cyclopentane-1,3-dione (Chem. Abstract, 43, 4908), 4,4-dimethylcyclopentane-1,3-dione (Chem. Abstract, 42, 4536e), etc.

Typical suitable 4-substituted urazoles including those represented by the formula:

III.



wherein R_1 represents a group selected from the class consisting of hydrogen; an alkyl, e.g., methyl, ethyl, propyl, butyl, amyl, octyl, decyl, dodecyl, benzyl, carboxyethyl, sulfopropyl, sulfobutyl, etc.; an aryl, e.g., phenyl, tolyl, naphthyl, etc.; R_2 represents a group selected from the class consisting of an alkyl, e.g., methyl, ethyl, octyl, dodecyl, benzyl, carboxylethyl, sulfopropyl, sulfobutyl, etc.; an aryl, e.g., phenyl, tolyl, naphthyl, etc.; and monoacyl and diacyl derivatives of compounds of Formula III, such as the mono- and di-acetyl, propionyl, butyryl, valeryl, caprylyl, capryl, and lauryl derivatives of such compounds. The exact structure of the acyl derivatives is not known.

Typical compounds of Formula III includes the following:

- (1) 4-phenyl urazole
- (2) 4-phenyl-1-ethyl urazole
- (3) 4-ethyl urazole
- (4) 4-phenyl urazole, diacetyl derivative
- (5) 4-(α -naphthyl)urazole
- (6) 4-octyl urazole

Many references are given in the chemical literature for the preparation of substituted urazoles. A method commonly used for the preparation of 4-substituted urazoles is heating biurea and an amine hydrochloride in the range of 180–240° C. 1-substituted urazoles can be prepared by heating substituted hydrazine hydrochlorides with urea at 150–200° C. Acyl derivatives can be prepared by acylation with anhydrides or acid chlorides.

The emulsions of our invention contain any of the higher speed silver halides such as silver bromoiodide, silver chlorobromide, and silver chlorobromoiodide desirably containing a predominate amount of bromide and a minor proportionate amount of iodide, (e.g., less than 10 mole percent) namely camera or high speed (e.g., A.S.A. generally greater than about 10) emulsions which are typically chemically sensitized with such addenda as sulfur sensitizers and gold sensitizers, dispersed in any of the hydrophilic colloids usually used in photographic emulsions including naturally occurring materials, e.g., gelatin, agar-agar, albumin, gum arabic, alginic acid, etc., and synthetic materials, e.g., polyvinyl alcohol, polyvinyl pyrrolidone, cellulose ethers, partially hydrolyzed cellulose acetate, etc.

The concentration of compounds of Formulas I and III used to advantage in our emulsions can be varied over a wide range. The carbocyclic 1,3-diones are more generally used at concentrations of from about 0.1 to about 5 g. per mole of silver halide. The 4-substituted urazoles are generally used in the range of from about 0.01 to about 5 g. per mole of silver halide. The optimum concentrations will depend upon the particular emulsion used, the particular compounds and the results desired, etc., and can be readily determined by methods well known in the art. For example, a concentration series is made using separate portions of the emulsion, coatings are made and exposed. One sample of each coating is then processed and a second sample incubated for a period of time before processing. The effect of concentration on sensitometric changes can then be readily determined.

The compounds of Formula I and III are advantageously added as a solution in any appropriate solvent, e.g.,

water, methanol, ethanol, propanol, acetone, pyridine, etc.

Our photographic silver halide emulsions can also contain such addenda as chemical sensitizers, e.g., sulfur, sensitizers (e.g., allyl thiocarbamide, thiourea, allylthiocyanate, cystine, etc.), various gold compounds (e.g., potassium chloroaurate, auric trichloride, etc.) (see U.S. patents such as Baldsiefen U.S. 2,540,085, issued Feb. 6, 1951, Damschroder U.S. 2,597,856, issued May 27, 1952, Yutzy et al. U.S. 2,597,915, issued May 27, 1952, etc.), various palladium compounds, such as palladium chloride (Baldsiefen et al. U.S. 2,540,086, issued Feb. 6, 1951), potassium chloropalladate (Stauffer et al. U.S. 2,598,079, issued May 27, 1952), etc., or mixtures of such sensitizers; spectral sensitizers 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; hardeners, such as formaldehyde (Miller U.S. 1,763,533, issued June 10, 1930), chrome alum (U.S. 1,763,533), dibromacrolein (British Patent 406,750), etc.; any of the color-forming couplers used in color photographic elements, such as the cyan-dye-forming couplers of Salminen et al. U.S. 2,313,586, issued March 9, 1943, Salminen U.S. 2,367,531, issued January 16, 1945, Salminen et al. U.S. 2,728,660, issued December 27, 1955, Salminen et al. U.S. 2,722,162, issued November 27, 1956, and many others, the magenta-dye-forming couplers, such as the couplers of Porter et al. U.S. 2,343,702 and 2,343,703, both issued March 7, 1964, Weissberger et al. U.S. 2,511,231, issued June 13, 1950, Feniak et al. U.S. 2,933,391, issued April 19, 1960, etc.; the yellow-dye-forming couplers of Vittum et al. U.S. 2,271,238, issued January 27, 1942, Porter et al. U.S. 2,289,805, issued July 14, 1942, McCrossen et al. U.S. 2,728,658, issued December 27, 1955, etc.; dispersing agents for couplers such as those set forth in Jelley and Vittum U.S. 2,322,027, Mannes et al. U.S. 2,304,940, issued December 15, 1942, etc. and other addenda commonly used in making emulsions for multicolor elements.

Our emulsions are coated to advantage by well known methods on any of the materials usually used including, for example, paper, glass, cellulose acetate, cellulose nitrate, other synthetic film forming resins, e.g., the polyesters, the polyamides, polystyrenes, etc.

Our multicolor elements are of the type described by Mannes et al. U.S. 2,113,329, issued April 5, 1938, which do not contain color-forming couplers or of the type containing the color-forming couplers which comprise a support coated with a red-sensitive silver halide emulsion containing a cyan-dye-forming coupler, a green-sensitive silver halide emulsion containing a magenta-dye-forming coupler, a bleachable yellow colored filter layer and a blue-sensitive silver halide emulsion containing a yellow-dye-forming coupler. The layers are often coated in the order listed, however the order can be varied provided the exposing light passes first through the blue-sensitive layer and then the yellow-colored filter layer. Additional filter layers, antihalation layers, etc., may be used to advantage in our elements.

The following examples will serve to still further illustrate our invention.

Example 1

A red-sensitive, high speed silver halide emulsion containing a phenolic cyan-dye-forming coupler was pre-

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pared as described in Example 6 of Carrol et al. U.S. Patent 2,944,900, issued July 12, 1960. Various amounts of 5,5-dimethylcycloalkane-1,3-dione as indicated in Table I were added to separate portions of this emulsion. Each portion was used to coat the red-sensitive layer in a multilayer color film of the type described in Example 16 of U.S. 2,944,900. Two samples of each of these multilayer coatings were exposed on an intensity scale sensitometer. One sample was processed fresh through a developer comprising:

G.	
N - ethyl- β -methanesulfoamidoethyl - 3 - methyl-4-aminoanilinesulfate	2.0
Sodium sulfite (anhydrous)	.6
Sodium carbonate (anhydrous)	30.0
Water to make 1.0 liter.	

stopped with a conventional acid stop bath, washed, then bleached in a conventional potassium ferricyanide bleach, fixed in a conventional sodium thiosulfate fix, washed and dried leaving a dye image. The other sample of coatings was incubated by holding them for two weeks at 78° F. and 50% R.H. and then processed as described above. The change in Log E (i.e. Log exposure) and the change in relative speed produced by storage of the film samples was determined and is summarized in the following table:

TABLE I

Concentration of 5,5-dimethylcyclohexane-1,3-dione in mg./mole of silver	2 weeks 78° F./50% RH vs. fresh coatings	
	Log E change	Relative speed change, percent
0	-.10	-20
120	-.07	-15
485	+.01	+2
970	+.02	+5

The results show that 485 mg. of 5,5-dimethylcyclohexane-1,3-dione per mole of silver in the red-sensitive cyan-dye-forming layer essentially eliminated any shift in Log E and change in relative speed produced by two week's incubation. Similar results are obtained with multilayer, multicolor photographic elements that do not contain incorporated couplers and which are developed in developing compositions such as are described in Mannes et al. U.S. 2,252,718, issued August 19, 1941, Vittum et al. U.S. 2,362,598, issued November 14, 1944, Vittum et al. U.S. 2,369,929, issued February 20, 1945, Porter et al. U.S. 2,439,098, issued April 6, 1948, Porter et al. U.S. 2,311,081, and 2,311,082 both issued February 16, 1943, Mannes et al. U.S. 2,113,330, issued April 5, 1938, Vittum et al. U.S. 2,271,238, issued January 27, 1942, etc.

Example 2

A series of multilayer color films on a cellulose acetate support was prepared as described in Example 1. The red-sensitive layer contained the 4-phenyl urazole listed in Table II. The coatings were exposed as described in Example 1. One set of the coatings was processed fresh as described in Example 1. The other set of coatings was incubated by holding for one week at 100° F. and 80% R.H. and then processed as described previously. The fog densities were measured and the amount of fog density produced by incubation is listed in Table II.

Table II

Conc. of 4-phenyl urazole in g./mole of silver:	Fog growth on incubation vs. fresh coatings
0	+.13
20	+.03
5	+.02

The results show that the presence in the silver emulsion of as little as 5 g. of 4-phenyl urazole per mole of silver almost eliminated the formation of fog produced by 1 week's incubation.

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Similarly, the 4-substituted urazoles are used to advantage in multilayer, multicolor elements that do not contain color-forming couplers for reducing the amount of fog produced by storage at high temperatures and humidities.

Example 3

A series of multilayer color films on a cellulose acetate support were prepared as described in Example 1. The green-sensitive emulsion layer contained a pyrazolone magenta-dye-forming coupler and also in certain cases contained 4-phenyl urazole. The coatings were exposed and processed as described in Example 1. Table III shows the results.

Table III

Conc. of 4-phenyl urazole in g.mole of silver:	Fog growth on incubation 1 week 100° F./80% RH vs. fresh coating
0	+.15
5	+.03

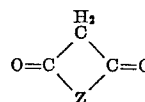
The results show that as little as 5 g. of 4-phenyl urazole per mole of silver in the emulsion containing magenta dye-forming coupler almost eliminated the formation of fog.

Similarly, any other of our cycloalkane-1,3-diones of Formula I and 4-substitute urazoles of Formula III are used to advantage in spectrally-sensitized photographic silver halide emulsions to minimize latent image changes and fog resulting from storage of an element containing said emulsion.

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 ejected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

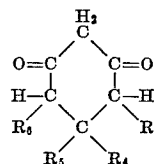
We claim:

1. A multicolor, multilayer photographic element containing at least one camera speed silver halide emulsion spectrally sensitized to light in the green or red region of the spectrum, said emulsion containing a carbocyclic-1,3-dione having the formula:



wherein Z represents the atoms required to complete a carbocyclic ring having from 5 to 6 carbon atoms in the nucleus such that the said ring is substituted with members selected from the class consisting of hydrogen, an alkyl group, an aryl group, a carbalkoxy group and the cyano group, the said carbocyclic 1,3-dione being incorporated to reduce latent image speed change.

2. A multicolor, multilayer photographic element containing at least one red-sensitized camera speed silver halide emulsion containing a cyan dye-forming coupler and a cycloalkane-1,3-dione having the formula:

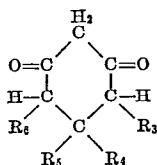


wherein R₃ and R₆ each represent a group selected from the class consisting of hydrogen, an alkyl, on aryl, cyano, and a carbalkoxy; and R₄ and R₅ each represent a group selected from the class consisting of hydrogen, an alkyl and an aryl, the said cycloalkane-1,3-dione being incorporated to reduce latent image speed change.

3. A multicolor, multilayer photographic element containing at least one gree-sensitized camera speed silver

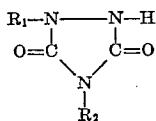
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halide emulsion containing a magenta dye-forming coupler and a cycloalkane-1,3-dione having the formula:



wherein R_3 and R_6 each represent a group selected from the class consisting of hydrogen, an alkyl, an aryl, cyano, and a carbalkoxy; and R_4 and R_5 each represent a group selected from the class consisting of hydrogen, an alkyl and an aryl, the said cycloalkane-1,3-dione being incorporated to reduce latent image speed change.

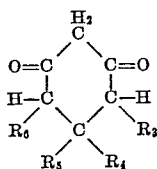
4. A photographic element as described in claim 1 wherein at least one of said silver halide emulsions contains a 4-substituted urazole having the formula:



wherein R_1 represents a group selected from the class consisting of hydrogen, an alkyl and an aryl; R_2 represents a group selected from class consisting of an alkyl group, and an aryl group, the said 4-substituted urazole being incorporated to reduce latent image fog growth.

5. A multicolor, multilayer photographic element containing at least one camera speed silver halide emulsion spectrally sensitized to light in the green or red region of the spectrum, said emulsion containing:

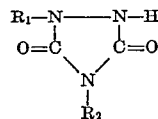
- (1) a dye-forming coupler,
- (2) a cycloalkane-1,3-dione having the formula:



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wherein R_3 and R_6 each represent a group selected from the class consisting of hydrogen, an alkyl, an aryl, cyano, and a carbalkoxy; and R_4 and R_5 each represent a group selected from the class consisting of hydrogen, an alkyl and an aryl; and

(3) a 4-substituted urazole having the formula:



wherein R_1 represents a group selected from the class consisting of hydrogen, an alkyl and an aryl; R_2 represents a group selected from the class consisting of an alkyl group, and an aryl group, the said cycloalkane-1,3-dione and said 4-substituted urazole being used as latent image stabilizers, the said cycloalkane-1,3-dione being used to reduce latent image speed changes and the said 4-substituted urazole being used to reduce latent image fog growth.

6. A photographic element of claim 5 in which the 4-substituted urazole is 4-phenyl urazole, and the cycloalkane-1,3-dione is 5,5-dimethylcycloalkane-1,3-dione.

7. A photographic element of claim 5 in which the 4-substituted urazole is 4-ethyl urazole, and the cycloalkane-1,3-dione is 5-phenylcycloalkane-1,3-dione.

8. A photographic element of claim 5 in which the 4-substituted urazole is 4-phenyl urazole, and the cycloalkane-1,3-dione is 5 - p - methoxyphenylcycloalkane-1,3-dione.

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40 J. TRAVIS BROWN, *Primary Examiner*.

U.S. Cl. X.R.

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