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3,677,761

DEVELOPMENT PROCESS

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No Drawing, Filed June 26, 1970, Ser. No. 50,314
Claims priority, application Great Britain, June 26, 1969, 32,426/69

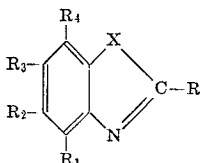
Int. Cl. G03c 1/06, 1/34, 5/30

U.S. Cl. 96—66.5

5 Claims

ABSTRACT OF THE DISCLOSURE

This invention describes a process for the production of a photographic record which comprises developing photographic material having a gelatino silver halide emulsion containing a developable silver image in a silver halide developing solution, the process being characterised in that it is carried out in the presence of a compound of the formula:



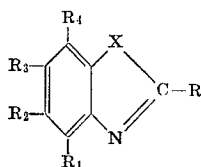
where X represents an oxygen, sulphur or selenium atom, R represents a hydrogen atom or an alkyl or substituted alkyl group, an aralkyl group, an aryl group or a group SR₅ where R₅ represents a hydrogen atom or an alkyl or substituted alkyl group, at least one of R₁, R₂, R₃ or R₄ is a nitro group and the remainder are each selected from a hydrogen or a halogen atom, or an alkyl, aralkyl, alkoxy, mono- or di-alkylamino, acylamino or a nitro group.

This invention relates to the processing of silver halide photographic film material and in particular to the processing of photographic film material under conditions which tend to give rise to a high fog level in the processed material.

It is usual to include an antifoggant in silver halide photographic developing solutions because the actual development process tends to cause fog in the developed material. The usual antifoggant employed in developing solutions is a water-soluble bromide. However under certain conditions it is required to use a stronger antifoggant than bromide and for this purpose a number of organic antifoggants have been used.

It is the object of the present invention to provide a photographic development process wherein certain novel antifoggants are used.

According to the present invention therefore there is provided a process for the production of a photographic record which comprises developing photographic material having a gelatino silver halide emulsion containing a developable silver image in a silver halide developing solution in the presence of a compound of the general formula:



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where X represents an oxygen, sulphur or selenium atom, R represents a hydrogen atom or an alkyl or substituted alkyl group, an aralkyl group, an aryl group, or a group SR₅ where R₅ represents a hydrogen atom or an alkyl or substituted alkyl group, at least one of R₁, R₂, R₃, or R₄ is a nitro group and the remainder are each selected from a hydrogen or a halogen atom, or an alkyl, aralkyl, alkoxy, mono- or di-alkylamino, acylamino or a nitro group.

It is preferred that the compounds of the above formula are present initially in the photographic material, most preferably in each silver halide emulsion layer. This is particularly the case when the photographic material is to be developed at an elevated temperature. An example of a photographic development process which employs an elevated temperature, i.e. a temperature above 30° C. is the so-called "rapid" method of processing X-ray films.

The "rapid" method comprises developing, washing and fixing the film material in solutions having an elevated temperature, usually 35° C. or above. The processing usually is carried out in a processing machine through which the photographic material is progressed by a roller system. For this reason it is usual to include in the developing solution a gelatin hardening agent such as glutaraldehyde, in order to prevent the swollen gelatin from being badly marked by the rollers. It has been found that such a process wherein the developing solution is at an elevated temperature and comprises a gelatin hardening agent tends to cause excessively high fog levels in photographic material processed therein. However when the photographic material comprises a compound of the formula hereinbefore set forth, the fog level in the developed material is reduced.

According to a particular embodiment of the present invention there is provided a process for the production of a photographic record which comprises developing a photographic material having a gelatino silver halide emulsion and containing a developable silver salt image at a temperature above 30° C. in a developing solution containing a gelatin hardening agent, the said photographic material containing in at least one emulsion layer or in a layer adjacent thereto a compound of the general formula hereinbefore defined.

The preferred gelatin hardening agent for use in this process is glutaric dialdehyde (glutaraldehyde) or a compound which comprises glutaric dialdehyde such as a bisulphite addition compound thereof.

The preferred amount of a compound of the above formula to be present in the emulsion of the photographic material for use in the process of the present invention is from 0.2 to 2 g. per gm. mole of silver halide present in the emulsion. It is preferred that a compound of the above formula is present in each emulsion layer of the photographic material. This is especially so in the case of X-ray film material wherein an emulsion layer is present on each side of the film support. The compounds of the above formula may however be present in a supercoat layer or in a sub-layer as long as this layer is adjacent to the emulsion layer.

However the compounds of use in the present invention may be present in the developing solution.

The following example will serve to illustrate the invention.

EXAMPLE

In this example compounds which fall within the above defined formula, as set forth in Table I which follows, were used. In Table I, the headings X, R, R₁, R₂, R₃ and R₄ refer to the symbols used in the formula as hereinbefore set forth.

TABLE I

Compound number	X	R	R ₁	R ₂	R ₃	R ₄
1.....	O	SCH ₃	H	NO ₂	H	H
2.....	S	H	H	H	NO ₂	H
3.....	S	SCH ₃	H	H	NO ₂	H
4.....	O	CH ₃	H	NO ₂	H	H
5.....	O	C ₆ H ₅	H	H	NO ₂	H
6.....	Se	CH ₃	H	CH ₃	NO ₂	H
7.....	Se	CH ₃	NO ₂	CH ₃	NO ₂	H
8.....	Se	CH ₃	NO ₂	CH ₃	H	H
9.....	Se	CH ₃	H	H	NO ₂	H
10.....	S	CH ₃	NO ₂ or H	CH ₃	CH ₃	H or NO ₂
11.....	Se	CH ₃	H	Br	NO ₂	H
12.....	Se	CH ₃	NO ₂ or H	CH ₃	CH ₃	N or NO ₂

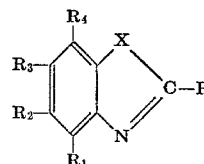
A sulphur and gold sensitised coarse-grained iodobromide emulsion of the type suitable for X-ray photography with intensifying screens was divided into two parts. To the first portion was added the usual coating aids and hardening agents. The second portion was treated similarly but in addition there was added the quantity specified in Table II (which follows) of the compound under test, dissolved in alcohol to form a 0.5% solution or dissolved in the requisite quantity of dilute sodium hydroxide solution. Each emulsion was coated on a flexible support in the conventional manner. After exposure through a wedge to a light source the spectral characteristics of which matched the emission from a calcium tungstate intensifying screen, the samples were processed in a conventional machine designed to process radiographs in a dry-to-dry time of 90 seconds: the development phase of this process was 25 seconds at 40° C. The developing solution used was a 1-phenyl-3-pyrazolidone/hydroquinone based developing solution which comprised g./litre of glutaric dialdehyde. The Table II records the data of fog, speed at a developed silver density of 1.0 and the average contrast over the density range of 0.2 to 2.0 for the control emulsion with no antifoggant and for the test emulsions containing the cited quantity of antifoggant per gm. mole of silver halide (the densities specified are measured from the fog density level and the speed figures are relative log speeds).

Compound number	Quantity in mg.	Fog	Speed	Average contrast
1.....	267	0.05	7.41	2.7
		0.14	7.66	2.3
2.....	267	0.05	7.33	2.7
		0.19	7.62	2.2
3.....	667	0.08	7.56	3.3
		0.30	7.87	2.9
4.....	1,000	0.13	7.69	2.5
		0.18	7.78	2.4
5.....	833	0.11	7.69	2.6
		0.18	7.78	2.4
6.....	33	0.09	7.66	2.9
		0.10	7.72	2.7
7.....	1,333	0.06	7.62	2.8
		0.09	7.70	2.7
8.....	1,333	0.06	7.61	2.8
		0.09	7.70	2.8
9.....	267	0.15	7.58	2.7
		0.20	7.62	2.5
10.....	33	0.15	7.58	2.7
		0.20	7.62	2.5
11.....	133	0.15	7.60	2.7
		0.18	7.65	2.6
12.....	27	0.13	7.46	2.6
		0.18	7.65	2.6

It is observed from this table that the control emulsions showed a high fog level and low contrast whereas the test emulsion, each containing a compound of the formula as hereinbefore set forth, have a relatively low fog and a high contrast. These qualities are particularly desired in radiographs.

We claim as our invention:

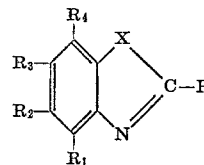
1. In a process for the production of a photographic record which comprises developing imagewise exposed photographic material having a gelatino silver halide emulsion containing a developable silver image in a silver halide developing solution, the improvement wherein the developing is carried out in the presence of a compound of the formula:



where X represents an oxygen, sulphur or selenium atom, R represents a hydrogen atom or an alkyl group, an aralkyl group, an aryl group or a group SR₅ where R₅ represents a hydrogen atom or an alkyl group, at least one of R₁, R₂, R₃ or R₄ is a nitro group and the remainder are each selected from a hydrogen or a halogen atom, or an alkyl, aralkyl, alkoxy, mono- or di-alkylamino, acylamino or a nitro group.

2. A process according to claim 1 wherein said compound in claim 1 is present in each silver halide emulsion layer of the photographic material.

3. In a process for the production of a photographic record which comprises developing an imagewise exposed photographic material having a gelatino silver halide emulsion and containing a developable silver salt image at a temperature above 30° C., in a developing solution containing a gelatin hardening agent, the improvement wherein the said photographic material contains in at least one emulsion layer or in a layer adjacent thereto a compound of the formula:



where X represents an oxygen, sulphur or selenium atom, R represents a hydrogen atom or an alkyl group, an aralkyl group, an aryl group or a group SR₅ where R₅ represents a hydrogen atom or an alkyl group, at least one of R₁, R₂, R₃ or R₄ is a nitro group and the remainder are each selected from a hydrogen or a halogen atom, or an alkyl, aralkyl, alkoxy, mono- or di-alkylamino, acylamino or a nitro group.

4. A process according to claim 3 wherein the gelatin hardening agent is glutaraldehyde or a compound which comprises glutaraldehyde.

5. A process according to claim 1 wherein R is hydrogen, methyl, phenyl or SCH₃; and R₁-R₄ are hydrogen, NO₂ or CH₃, at least one of R₁-R₄ being NO₂.

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U.S. Cl. X.R.