

[54] **HIGH TEMPERATURE PROCESSING OF PHOTOGRAPHIC SILVER HALIDE ELEMENTS**

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[58] Field of Search **96/48 QP, 63, 66, 66.3, 96/66.5, 109, 95**

[56] **References Cited**

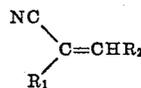
UNITED STATES PATENTS

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[57] **ABSTRACT**

A method for producing photographic images by development of an exposed silver halide element at elevated temperature is provided wherein the development occurs in the presence of a nitrile compound selected from the group consisting of: (a) benzene compounds carrying at least 2 cyano groups, (b) π -deficient heterocycles carrying at least 1 cyano group on the heterocyclic nucleus, and (c) compounds carrying at least one cyano group on an olefinic group, which correspond to the formula:



wherein: R₁ is a cyano group or a π -deficient heterocycle, and R₂ is an aryl group, a substituted aryl group, a heterocycle or a substituted heterocycle.

The nitrile compounds have a favourable effect on the sensitometric properties of the silver halide emulsion that are developed at elevated temperature. They reduce the supplemental fog produced by development at elevated temperature.

9 Claims, No Drawings

HIGH TEMPERATURE PROCESSING OF PHOTOGRAPHIC SILVER HALIDE ELEMENTS

The present invention relates to the development at increased temperature of exposed photographic radiation sensitive silver halide elements.

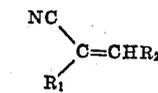
In normal processing of exposed photographic materials development is carried out at ambient temperature (about 20° C) and requires a relatively long time say several minutes. Therefore, there is a general trend to enhance the speed of processing, which can be done by carrying out development and the other processing operations at elevated temperatures. Rapid development of photographic elements occurs at temperatures above 30° C and preferably between 35° and 45° C.

When the processing of exposed photographic silver halide elements is carried out at elevated temperatures i.e., above 30° C these elements have a tendency of showing increased fog and generally the other sensitometric characteristics are impaired also.

It is known to reduce the formation and growth of fog in photographic silver halide elements by means of antifoggants or stabilizers e.g. heterocyclic mercapto compounds such as 1-phenyl-5-mercapto-tetrazole and azaindenes, more particularly tetra- or pentaazaindenes, especially those substituted by hydroxy or amino groups e.g. 5-methyl-7-hydroxy-s-triazolo-[1,5-a]pyrimidine. The latter compounds are used to stabilize the emulsion against formation and growth of fog when the photographic materials are stored before use. The compounds have only a relatively weak effect in reducing fog formation when the photographic materials are used immediately after preparation. 1-Phenyl-5-mercaptotetrazole, on the contrary, has a high fog-reducing effect immediately after the preparation of the photographic emulsions. Therefore, both compounds are generally used together in the emulsion.

However, the supplemental fog produced by the processing at elevated temperatures cannot be reduced sufficiently by means of the conventional antifoggants or stabilizers.

It has now been found that nitrile compounds selected from the group consisting of (a) benzene compounds carrying at least two cyano groups on the benzene nucleus (b) π -deficient heterocycles e.g. pyridine, quinoline, isoquinoline, etc. carrying at least one cyano group on the heterocyclic nucleus and (c) compounds carrying at least one cyano group on an olefinic group and corresponding to the formula:



wherein:

R₁ stands for a cyano group or a π -deficient heterocycle, and

R₂ represents an aryl group including a substituted aryl group or a heterocycle, e.g. furyl, thienyl, indolyl, indolynyl, benzimidazolyl, etc. including a substituted heterocycle,

have a favourable effect on the sensitometric characteristics i.e., fog and/or speed and/or gradation of light-sensitive silver halide emulsions, which after exposure are processed at elevated temperature. They generally reduce the supplemental fog formed without reducing

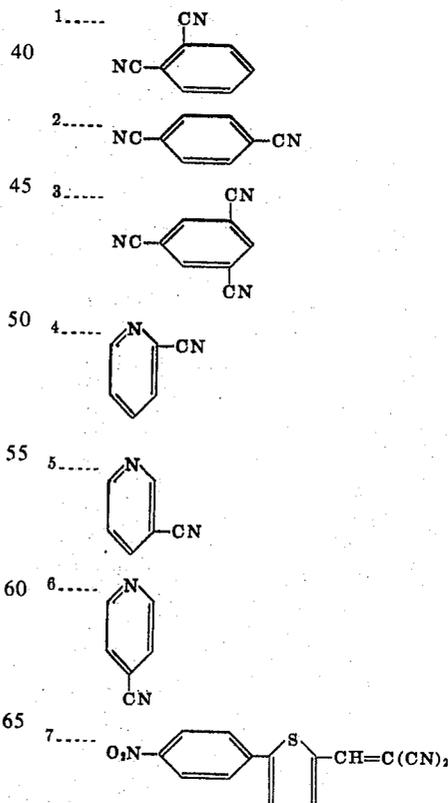
the emulsion speed to a noteworthy extent or even in some cases with an increase of the emulsion speed. Other compounds give rise to an increase of the speed and/or gradation without showing a noteworthy influence on the fog.

As is known by those skilled in the art of organic chemistry and, as can be learned from A. Albert "Heterocyclic Chemistry" pages 34 and 39, University of London, The Athlone Press, 1959, π -deficient heterocycles are completely unsaturated heterocycles having nitrogen as the sole hetero-element and a deficit of π -electrons elsewhere, more particularly heterocycles derived from carbocyclic aromatic ring systems wherein one or more =CH- groups are replaced by =N- groups.

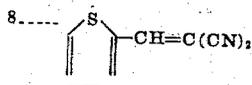
Thus, the present invention provides a method of producing photographic images, which comprises developing an exposed photographic element comprising a support and at least one photographic silver halide emulsion, at a temperature above 30° C wherein the said development is carried out in the presence of at least one nitrile compound as defined above.

The nitrile compounds of use according to the invention are particularly useful in photographic silver halide materials, which are stabilized against formation and growth of fog by means of azaindene compounds as described above and therefore the present invention also provides light-sensitive silver halide materials, which comprise an azaindene stabilizer, especially 5-methyl-7-hydroxy-s-triazolo-[1,5-a]pyrimidine, and a nitrile compound as defined above.

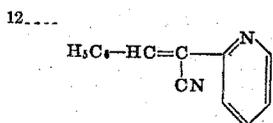
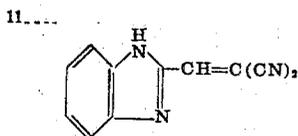
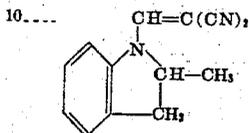
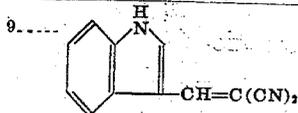
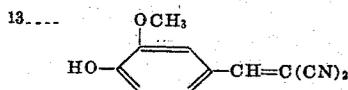
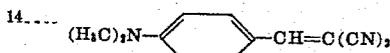
The following are representative examples of nitrile compounds which were found particularly suitable for use according to the present invention. Where deemed necessary, literature references are given as to the preparation of these compounds.



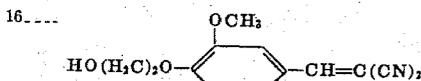
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(1928).

Compound 7 was prepared as follows:

A mixture of 43.4 g (0.2 mole) of 5-(p-nitrophenyl)-2-furaldehyde (Sb.Pr.Chem.Fak. SVST (Slov.Vys.Sk. Techn.) 1962, 35), 13.2 g (0.2 mole) of malodinitrile, 0.5 g of ammonium acetate and 0.5 g of acetamide in 150 ml of acetic acid was refluxed for 2 hours. The precipitate formed was filtered off by suction and recrystallized from ethylene glycol monomethyl ether. Yield: 32 g (60 percent). Melting point: 222°-223° C.

Compound 9 was prepared as follows:

A mixture of 29 g (0.2 mole) of indole-3-carbaldehyde (Org.Syn.Coll.Vol. 4, 539), 13.2 g (0.2 mole) of malodinitrile, 0.5 g of ammonium acetate and 0.5 g of acetamide in 80 ml of acetic acid was refluxed for 1 hour. The precipitate formed was filtered by suction and recrystallized from ethylene glycol monomethylether/water (2:1). Yield: 26 g (67 percent). Melting point: 229°-230° C.

Compound 10 was prepared as follows:

A solution of 13.3 g (0.1 mole) of 2-methylindoline 14.8 g (0.1 mole) of ethyl orthoformate and 6.6 g (0.1 mole) of malodinitrile in 150 ml of ethylene glycol

monomethyl ether was refluxed for 30 minutes. The reaction mixture was poured into water and the precipitate was filtered off by suction. After washing with water it was recrystallized from methanol.

5 Yield: 11 g (52 percent). Melting point: 155° C.

Compound 11 was prepared as follows:

A suspension of 29.2 g (0.2 mole) of benzimidazole-2-carboxaldehyde (Chem.Ber. 98, 1330 (1965), 13.2 g (0.2 mole) of malodinitrile, 0.5 g of ammonium acetate and 0.5 g of acetamide in 200 ml of acetic acid, was refluxed for 2 hours with stirring. The precipitate formed was filtered off and boiled with ethylene glycol monomethyl ether. The filtrate was poured into water and the precipitate after having been filtered off by suction 15 was washed with ether.

Yield: 6 (g percent). Melting point: above 260° C.

Compound 16 was prepared as follows:

A mixture of 39.2 g (0.2 mole) of 3-methoxy-4-β-hydroxyethoxybenzaldehyde, prepared as described below, 13.2 g (0.2 mole) of malodinitrile, 0.5 g of ammonium acetate and 0.5 g of acetamide in 80 ml of acetic acid, was refluxed for 2 hours. The precipitate formed was filtered off by suction and recrystallized from toluene.

25 Yield: 21.5 g (44 percent). Melting point: 148° C.

The 3-methoxy-4-β-hydroxyethoxybenzaldehyde was prepared as follows:

A mixture of 76 g (0.5 mole) of 3-methoxy-4-hydroxybenzaldehyde, 80.5 g (1 mole) of 2-chloroethanol, and 106 g (1 mole) of sodium carbonate in 500 ml of diethylformamide was refluxed for 1 hour with stirring. The mixture was concentrated by evaporation and the residue recrystallized from benzene.

35 Yield: 67 g (69 percent). Melting point: 98° C.

While the nitrile compounds used in accordance with the present invention may be present in any of the water-permeable colloid layers of the photographic material, which are in water-permeable relationship with the silver halide emulsion layer e.g. a gelatin antistress layer, an intermediate layer, a filter layer, etc.

It is a particularly useful form of the invention to incorporate the nitrile compounds into the silver halide emulsion itself.

45 The preparation of the silver halide emulsions involves three separate operations:

1. the emulsification and digestion or ripening of the silver halide,
- 50 2. the freeing of the emulsion from water-soluble salts usually by washing, and
3. the second digestion or after ripening (chemical ripening) to obtain increased sensitivity.

The compounds of use according to the present invention can be added to the emulsion during no matter what step of emulsion preparation, preferably just before the coating of the emulsion on a suitable support, e.g. paper, glass, or film such as cellulose triacetate and polyethylene terephthalate.

The compounds of use according to the invention can be used with any type of light-sensitive material that after exposure is intended to be processed at elevated temperature. Various silver salts can be used as light-sensitive salt, e.g. silver bromide, silver iodide, silver chloride or mixed silver halides, e.g. silver chlorobromide or silver bromiodide. They are particularly valuable to improve the fog on rapid processing at elevated temperature of medium or high-speed image

forming silver halide emulsions, in which the silver halide is predominantly silver bromide, e.g. silver bromoiodide emulsions, the iodide content of which is generally less than 10 mole percent.

The silver halides are dispersed in the common hydrophilic colloids such as gelatin, casein, zein, polyvinylalcohol, carboxymethyl cellulose, alginic acid etc. gelatin being, however, favoured.

The silver halide emulsions for being processed after exposure at elevated temperature generally are silver halide emulsions having a low content of hydrophilic colloid e.g. gelatin. The ratio of hydrophilic colloid, more particularly gelatin, to silver halide expressed as silver nitrate is generally comprised between 0.2 and 0.6.

The compounds of use according to the invention may be used in amounts varying between very wide limits. The optimum amount for each individual compound can be easily determined by some simple test known to those skilled in the art. In the silver halide emulsion they are generally employed in amounts comprised between 1 mg and 1,000 mg per mole of silver halide.

The silver halide emulsions can be sensitized chemically as well as spectrally.

They can be sensitized chemically by any of the accepted procedures. The emulsions can be digested with naturally active gelatin or sulphur compounds, e.g. allyl thiocyanate, allyl thiourea, sodium thiosulphate etc. The emulsions can be sensitized also by means of reductors, e.g. tin compounds as described in U.K. Pat. Specification 789,823 and by means of small amounts of noble metal compounds, e.g. of gold, platinum, palladium, iridium, ruthenium, and rhodium as described by R. Koslowsky, *Z. Wiss. Phot.* 46, 67-72 (1951). Representative noble metal compounds are ammonium chloropalladate, potassium chloroplatinate, potassium chloroaurate, and potassium aurithiocyanate. Of course, the emulsions can also be sensitized chemically with a combination of the above chemical sensitizers.

The emulsions may further comprise compounds that sensitize the emulsion by development acceleration, e.g. alkylene oxide polymers. These alkylene oxide polymers may be of various type, e.g. polyethylene glycol having a molecular weight of 1,500 or more, alkylene oxide condensation products or polymers as described in U.S. Pat. Nos. 1,970,578 — 2,240,472 — 2,423,549 — 2,441,389 — 2,531,832 and 2,533,990 and in U.K. Pat. Specifications 920,637 — 940,051 — 945,340 — 991,608 and 1,015,023. These development accelerating compounds may also be present in the silver halide developing solution. Other development accelerating compounds are onium and polyonium compounds preferably of the ammonium, phosphonium, and sulphonium type.

The emulsions can be sensitized spectrally, e.g. by means of the common methine dyes such as neutrocyanines, basic or acid carbocyanines, rhodacyanines,

hemicyanines, styryl dyes, oxonol dyes and the like. Such spectrally sensitizing dyes have been described by F. M. Hamer in "The cyanine dyes and related compounds" (1954).

The common emulsion stabilizers or antifoggants can be added to the silver halide emulsions or the developing bath. Known antifoggants or stabilizers are, e.g. sulphinic and selenic acid or salts thereof, aliphatic, aromatic or heterocyclic mercapto compounds or disulphides, e.g. benzothiazoline-2-thione and 1-phenyl-5-mercaptotetrazole which may comprise sulpho groups or carboxyl groups, nitroindazole, nitrobenztriazole, nitrobenzimidazole, mercury compounds, e.g. those described in Belgian Pat. Nos. 524,121 — 677,337 — 707,386 and 709,195 and as already noted above azaindenes, particularly the tetra- or pentaazaindenes and especially those substituted by hydroxy- or amino groups as described by Birr in *Z. Wiss. Phot.* 47, 2-58 (1952).

Other addenda, e.g. hardening agents such as formaldehyde, mucochloric and mucobromic acid, dialdehydes, etc. wetting agents, e.g. the fluorinated surfactants of U.K. Pat. Application No. 58431/68, plasticizers, matting agents e.g. polymethyl methacrylate and silica particles, colour couplers, mask-forming compounds, light-screening dyes etc. may be present in the silver halide emulsion or another layer of the light-sensitive materials of the invention.

The following examples illustrate the present invention:

Example 1

A silver bromoiodide X-ray emulsion ready for coating comprises per kg an amount of silver halide corresponding to 190 g of silver nitrate, 74 g of gelatin, 545 mg of 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine, 6.5 mg of 1-phenyl-5mercaptotetrazole, and 0.45 mg of mercury cyanide.

The above emulsion was divided into several aliquot portions and to each of these portions one of the nitrile compounds listed in the table below was added in the amount given.

The emulsion portions were coated on a polyethylene terephthalate support and dried.

After exposure through a continuous wedge with constant 0.15 the emulsions were processed in an automatic 90 seconds processing machine. Development occurred for 23 seconds at 35° C in Agfa-Gevaert's hardening developer for automatic machine processing G 138 which comprises hydroquinone and 1-phenyl-3-pyrazolidinone as developing agents and glutaraldehyde as hardener.

The sensitometric results obtained with the fresh materials and with materials that were stored before exposure and processing for 5 days at 45° C and 70 percent relative humidity are listed in the table below. The values given for the speed are relative values measured at density 1 above fog; a value of 100 has been given to the speed of the fresh material comprising no suitable compound.

Table

mg nitrile compound per kg emulsion	Fresh material			Stored material		
	Fog	Speed	amma	Fog	Speed	amma
—	0.21	1.52	100	0.27	1.32	112
10 mg of compound 3	0.17	1.47	91	0.21	1.24	107
100 mg of compound 3	0.20	1.53	98	0.22	1.35	117

Table—Continued

mg nitrile compound per kg emulsion	Fresh material			Stored material		
	Fog	amma	Speed	Fog	amma	Speed
	10 mg of compound 6	0.20	1.54	102	0.23	1.38
10 mg of compound 9	0.18	1.32	89	0.22	1.16	81
10 mg of compound 10	0.17	1.33	83	0.20	1.21	87
100 mg of compound 10	0.19	1.61	89	0.23	1.33	86
10 mg of compound 13	0.19	1.42	86	0.22	1.19	102
100 mg of compound 13	0.19	1.46	86	0.21	1.27	105
10 mg of compound 14	0.18	1.48	91	0.21	1.29	98
100 mg of compound 14	0.19	1.65	87	0.27	1.91	120

The above results show that the compounds used according to the invention have a favourable fog-reducing effect when processing at elevated temperature. Some compounds have a favourable effect on the gradation (compound 14) and speed (compounds 3, 6 and 14) after storage.

Example 2

Example 1 was repeated with the difference that now the nitrile compound listed in the table below was used.

The following sensitometric results were obtained.

Table

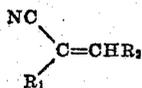
mg nitrile compound per kg emulsion	Stored material		
	Fog	Gamma	Speed
—	0.16	0.74	100
100 mg of compound 11	0.15	0.84	182

The above results show the favourable effect of compound 11 on the fog, gradation as well as the speed of the material, which was processed at elevated temperature after having been stored for 5 days at 45° C and 70 percent relative humidity.

We claim:

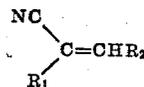
1. Method of producing photographic images, which comprises developing an exposed photographic element comprising a support and at least one photographic silver halide emulsion, at a temperature above 30°C, wherein the said development is carried out in the presence of at least one nitrile compound selected from the group consisting of:

- benzene compounds carrying at least 2 cyano groups on the benzene nucleus
- π -deficient heterocycles carrying at least 1 cyano group on the heterocyclic nucleus, and
- compounds carrying at least one cyano group on an olefinic group, which correspond to the formula:



wherein:

- R_1 is a cyano group or a π -deficient heterocycle, and R_2 is an aryl group or a heterocycle.
- Method according to claim 1, wherein the said nitrile compound is present in a silver halide emulsion.
- Method according to claim 2, wherein the said nitrile compound is present in an amount comprised between 1 mg and 1000 mg per mole of silver halide.
- Method according to claim 1, wherein the emulsion comprises an azaindene emulsion stabilizer.
- Method according to claim 4, wherein said azaindene emulsion stabilizer is 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine.
- A light-sensitive photographic silver halide material, which comprises besides an azaindene emulsion stabilizer at least one nitrile compound selected from the group consisting of:
 - benzene compounds carrying at least two cyano groups,
 - π -deficient heterocycles carrying at least one cyano group on the heterocyclic nucleus, and
 - compounds carrying at least one cyano group on an olefinic group, which correspond to the formula:



wherein:

- R_1 is a cyano group or a π -deficient heterocycle, and R_2 is an aryl group or a heterocycle.
- A light-sensitive photographic silver halide material according to claim 6, wherein said nitrile compound is present in a gelatino silver halide emulsion in an amount comprised between 1 mg and 1,000 mg per mole of silver halide.
- A light-sensitive photographic material according to claim 7, wherein the ratio of gelatin to silver halide expressed as silver nitrate in the emulsion is comprised between 0.2 and 0.6.
- A light-sensitive material according to claim 6, wherein the azaindene emulsion stabilizer is 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine.

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