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# LITH-TYPE OF EMULSION CONTAINING PYROZOLONE

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U.S. Cl. 96—95 2 Claims

## ABSTRACT OF THE DISCLOSURE

A Lith-Type emulsion which has improved contrast and halftone dot quality. A pyrazolone compound is incorporated with an alkylene oxide in a silver halide emulsion.

This invention relates to light-sensitive photographic silver halide materials and particularly to photographic printing materials of the "lith-type."

A light-sensitive photographic silver halide material which is used for halftone reproduction in the recent graphic arts is called as a "lith-type" film, for which are required various photographic properties including high image contrast, sharp halftone dots and good line image, broad latitude for development, high speed and high resolution.

In the graphic arts, therefore, use of an infectious developing solution which is an alkaline hydroquinone developer containing an aldehyde has been proposed for development of the "lith-type" film in order to obtain high image contrast and sharp halftone dots. Detailed information for this will be available from the article entitled "Formaldehyde Hydroquinone Developer and Infectious Development" in Journal of the Franklin Institute Volume 239, page 221 et seq. (1945). Halftone dots obtained by use of said infectious developer are very hard and sharp. However, if the above results are obtained, a "lith-type" emulsion used should originally have high contrast.

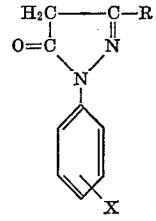
In order to obtain high contrast and good halftone dot quality, various methods have been employed. In German Pat. No. 1,122,834 and Journal of Photographic Science Vol. 12, page 5 (1964), for example, a method of obtaining a halftone dot image with high contrast by using a "lith-type" emulsion incorporated with an alkylene oxide compound is disclosed. In this method, however, the formation of halftone dots with high contrast takes place only at the later stage of infectious development. At the earlier stage, considerable decrease of photographic speed and contrast as well as poor halftone dot quality are observed. In order to avoid this drawback, addition of a quarternary alkyl amine together with an alkylene oxide compound into the "lith-type" emulsion can be made. By this method, photographic speed and halftone dot quality at the earlier stage can be improved. At the stage after a normal period of development, however, halftone dot quality is greatly degradated. Thus it is difficult to obtain good halftone dot quality over the entire period of development.

Accordingly, the object of this invention is to provide a light-sensitive photographic silver halide material which has excellent photographic properties at the initial stage of infectious development and good contrast and halftone dot quality even at the stage after a normal period of development.

In accordance with the present invention, there is provided a light-sensitive silver halide photographic material comprising a support and a light-sensitive emulsion



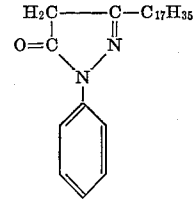
layer coated thereon, characterized by a compound of the general formula



(wherein R is acylamino, arylamino, alkyl, aryl or aralkyl radical and X is hydrogen atom or carboxyl or sulfonic group) is incorporated together with an alkylene oxide compound (molecular weight 600–8,000) in the light-sensitive emulsion layer or in the layer contiguous therewith.

Examples of pyrazolone compounds used in this invention include the following ones without limitation thereto.

[1]



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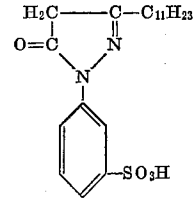

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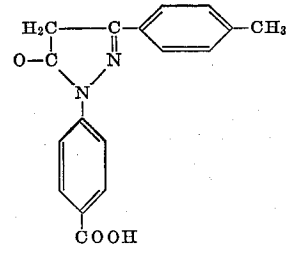

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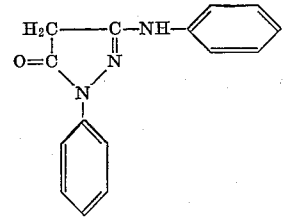

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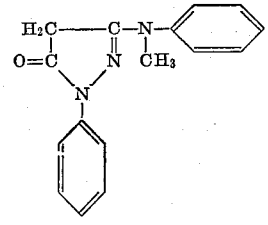
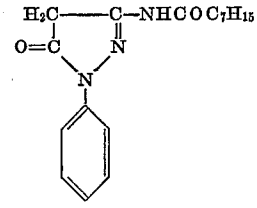
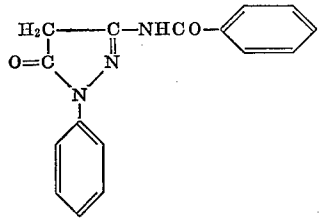
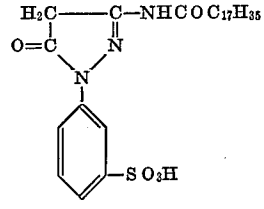
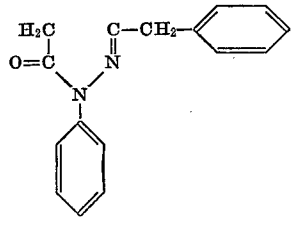


[6] 

[7] 

[8] 



As the alkylene oxide compounds referred to therein may be included the condensation products of alkylene oxide with water, aliphatic alcohols, glycols, fatty acids, aliphatic amines, phenols, hexitol ring dehydration products, etc. These alkylene oxide compounds may be used singly or in combination.

The amounts of the pyrazolone and alkylene oxide compounds to be added will vary depending on their types. Preferably the pyrazolone compound is used in an amount of 10 mg. to 10 g. per one mole of silver halide and the alkylene oxide compound used in an amount of 10 mg. to 10 g. per one mole of silver halide.

The pyrozolone compound and the alkylene oxide compound may be added to the light-sensitive silver halide emulsion at any stage during the preparation of said emulsion. But the most preferable result is obtained when these compounds are added after ripening and before coating of said emulsion. The compounds to be added can be introduced in the form of a solution in aqueous sodium hydroxide or in an organic solvent such as methanol. The solution may be incorporated in a photographic layer adjacent to the emulsion layer, e.g. in a protective layer or an inter layer.

In the present invention, any type of silver halide emulsions are usable. For example, silver chloride, bromide and iodide emulsions or their mixtures are usable. Further, these emulsions may be sensitized chemically by sulfur sensitization (with ammonium thiosulfate), gold sensitization (with gold chloride) or optical sensitization (with cyan dye or merocyan dye). Suitable hardening agents and surface active agents can be added to the emulsion. The silver halide is dispersed in hydrophilic materials used as binders such as gelatine or polyvinyl alcohol. The material of the invention can be treated with a conventionally known "lith-developer."

As stated hereinabove, a light-sensitive silver halide photographic material of this invention is useful as a "lith-type" film which has good image contrast, sharp



halftone dots and line image, good latitude for development and high photographic speed and high resolution.

The present invention is illustrated in the following example but not limited thereto.

## EXAMPLE

A gelatinous silver chlorobromide emulsion containing 20 mole percent silver bromide was divided into separate ten portions, one of which was used as such for the preparation of control films and the remaining nine were added respectively with various compounds specified in the table below. Each of the emulsions thus prepared were coated on a film base and then dried. The films thus obtained were tested in sensitometry and evalution of halftone dot quality.

In the sensitometry, the individual film to be tested was brought into close contact with a step-wedge and then subjected to exposure to irradiation through the step-wedge from an iodine lamp of 200 volt and 1 kw. as a light source. The exposed film was then treated with a developing solution described hereafter. In this test, relative speed was determined at the point where the density is 1.0.

In the evaluation of halftone dot quality, the film to be tested was brought into contact with a magenta contact screen under suction in vacuum. Exposure to light and development were carried out in the same manner as in the above-mentioned sensitometry. The amount of the light exposure, however, was regulated so as to produce dot size 40–60%. The halftone dots formed were visually inspected by means of a microscope. Rating of halftone dot quality was made in term of sharpness. Rating "5" indicates that the dots have the highest sharpness, while rating "1" does that the dots have the lowest sharpness. Halftone dots between these two ratings are classified to ratings 4, 3 and 2.

The additives used in this example are shown in the following table.

| Sample | Additive (quantity added per 0.5 mole of silver halide) | | |
|---|---|---|---|
| 1 | | Control | |
| 2 | Alkylene oxide compound alone. | Polyethylene glycol (molecular weight: 1,000), g. | 1 |
| 3 | | Polyethylene glycol (molecular weight: 4,000), g. | 0.05 |
| 4 | | Condensate of ethylene oxide (molecular weight: 900) and lauryl alcohol, g. | 0.4 |
| 5 | Pyrazolone compound alone. | Compound 3, g. | 0.1 |
| 6 | | Compound 5, g. | 0.05 |
| 7 | | Compound 7, g. | 0.08 |
| 8 | Joint use of alkylene oxide compound and pyrazolone compound. | Polyethylene glycol (M.W. 4,000), g. | 0.05 |
| | | Compound 3, g. | 0.1 |
| 9 | | Polyethylene glycol (M.W. 1,000), g. | 1 |
| | | Compound 5, g. | 0.05 |
| 10 | | Condensate of ethylene oxide (M.W. 900) and lauryl alcohol, g. | 0.4 |
| | | Compound 7, g. | 0.08 |

Developing treatment was carried out at 20° C. stepwise for 1.5 minutes, 2.5 minutes and 3.5 minutes by using the developing solution having the following composition:

Warm water—500 cc.
Additive product of formaldehyde and sodium sulfite—50 g.
Hydroquinone—19 g.
Sodium carbonate—80 g.
Boric acid—10 g.
Potassium bromide—2.2 g.
Water to make up 1000 cc.

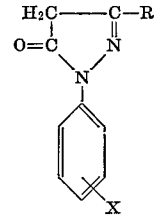
Below are the results obtained.

| Sample | | Relative speed, minutes 1.5 | 2.5 | 3.5 | Evaluation of halftone dot, minutes 1.5 | 2.5 | 3.5 |
|---|---|---|---|---|---|---|---|
| 1 | | 100 | 190 | 250 | 2 | 1 | 1 |
| 2 | Alkylene oxide compound alone. | 30 | 60 | 100 | 2 | 3 | 4 |
| 3 | | 10 | 40 | 100 | 1 | 2 | 4 |
| 4 | | 10 | 35 | 90 | 1 | 2 | 4 |
| 5 | Pyrazolone compound alone. | 53 | 170 | 250 | 2 | 2 | 1 |
| 6 | | 75 | 190 | 250 | 2 | 2 | 1 |
| 7 | | 64 | 175 | 230 | 2 | 2 | 1 |
| 8 | Alkylene oxide compound and pyrazolone compound. | 42 | 93 | 140 | 3 | 5 | 4 |
| 9 | | 60 | 105 | 140 | 3 | 4 | 4 |
| 10 | | 50 | 90 | 130 | 3 | 3 | 4 |

As noted from the above table, the Samples 2, 3 and 4 to which only an alkylene oxide compound is added show decrease in sensitivity and halftone dot quality in the initial development. The samples 5, 6 and 7 to which only a pyrazolone compound is added show less decrease in sensitivity than that observed in the above alkylene oxide addition samples, whereas the halftone dot quality decreased. On the contrary, sensitivity and halftone dot quality of the samples 8, 9 and 10 in which an alkylene oxide derivative and a pyrazolone compound are included together according to the present invention, are remarkably recovered. The halftone dot quality of these samples do not show any decrease even after the treatment for 3.5 minutes.

What is claimed is:

**1.** A light-sensitive photographic silver halide material of the "lith-type," which comprises a support and a light-sensitive photographic silver halide emulsion layer coated thereon, a pyrazolone compound of the formula



wherein R is an acylamino, arylamino, alkyl, aryl or aralkyl group and X is hydrogen atom, a carboxyl or a sulfonic acid group; and a condensation product of an alkylene oxide and a compound selected from the group consisting of water, an aliphatic alcohol, a glycol, an aliphatic acid, an aliphatic amine, a phenol and a hexitol ring dehydration product; said pyrazolone compound and condensation product are both contained in the emulsion layer or a layer adjacent thereto.

**2.** A light-sensitive photographic silver halide material of the "lith-type" as claimed in claim **1**, wherein said pyrazolone compound and said condensation product are used in the individual amount of 10 mg. to 10 g. per one mole of silver halide contained in said emulsion.


**References Cited**

UNITED STATES PATENTS

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|---|---|---|---|
| 2,848,330 | 12/1955 | Chechak et al. | 96—107 |
| 3,214,437 | 4/1960 | Loria et al. | 96—100 |



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U.S. Cl. X.R.

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