

- [54] **DEVELOPER COMPOSITION FOR LITHOGRAPHIC PRINTING PLATES**
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- [52] U.S. Cl..... **96/66.4, 96/66 R**
- [51] Int. Cl..... **G03c 5/30**
- [58] Field of Search..... 96/66, 66.4

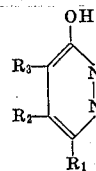
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Primary Examiner—Mary F. Kelley
Attorney, Agent, or Firm—Eric H. Waters

[57] **ABSTRACT**

A developer formulation for silver halide-containing lithographic printing plates which comprises an infectious developer containing hydroquinone as developing agent and, incorporated therein, a compound of the formula:



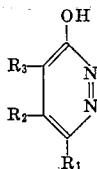
wherein R₁ is a hydrogen atom, an alkyl group, a hydroxy group or a carboxy group; R₂ is a hydrogen atom, an alkyl group, a halogen atom, or a carboxyalkyl group; and R₃ is a hydrogen atom, a cyano group, a halogen atom or a carboxy group, provided that R₂ and R₃ may bond together to form a benzene ring.

2 Claims, No Drawings

DEVELOPER COMPOSITION FOR LITHOGRAPHIC PRINTING PLATES

This invention relates to a developer formulation for silver halide-containing lithographic printing plates which comprises an infectious developer containing hydroquinone as developing agent and, incorporated therein, a compound of the general formula shown below, and aims to overcome the degradation in infectious developability of the infectious developer which is caused by oxidation of the hydroquinone contained therein.

General Formula:



wherein R₁ is a hydrogen atom, an alkyl group, a hydroxy group or a carboxy group; R₂ is a hydrogen atom, an alkyl group, a halogen atom, or a carboxy-alkyl group; and R₃ is a hydrogen atom, a cyano group, a halogen atom or a carboxy group, provided that R₂ and R₃ may bond together to form a benzene ring.

Generally, a lithographic printing master plate bearing a linear or dot image is obtained by developing a lith-type photosensitive material with an infectious developer, which is a hard tone developer. The infectious developer contains hydroquinone as developing agent and, in addition thereto, sodium sulfite and paraformaldehyde. It is considered that the said components bring about such reaction as $\text{CH}_2\text{O} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} = \text{CH}_2\text{O} \cdot \text{NaSO}_3 + \text{NaOH}$ to make the developer extremely low in free sulfite ion concentration. If the infectious developer with the low sulfite concentration is used, the active hydroquinone (semiquinone) in the developer is rather safe from the attack by sulfite ion retaining its active state over a long period of time. Thus, replenishment of activated hydroquinone is possible for a long period, and so the developed image can be made hard in tone. However, the above-mentioned infectious developer containing hydroquinone as developing agent which is low in sulfite ion concentration has the disadvantage that the hydroquinone is readily oxidized with lapse of time after preparation of the developer, with the result that the developer is deprived of its infectious developability. The known infectious developer having the above-mentioned disadvantage is not satisfactory in practice, and has been required to be improved in storability.

In view of the above, facts we made extensive studies and discovered that when a compound of the aforesaid general formula is added to an infectious developer, the hydroquinone contained in the developer is greatly improved in stability to make it possible to prevent the developer from degradation in infectious developability.

It is therefore an object of the present invention to provide an infectious developer formulation containing hydroquinone as developing agent in combination with an addition product of aldehyde and alkali hydrogen sulfite or an addition product of cyclohexane or acetone and a soluble sulfite. That is, the present invention provides an infectious developer composition containing hydroquinone as developing agent in combination with a compound having a carbonyl group ($> \text{C}=\text{O}$)

and with a soluble sulfite, to which developer composition has been added the aforesaid compound of the present invention in a proportion of 0.1 to 50 g. per liter of the developer. The compound according to the present invention may be added in a proportion of more than 50 g. per liter of the developer. Even if the compound is added in such a large amount as above, however, the practical effect is not increased as much.

Typical examples of the compound used in the present invention are shown below, but compounds usable in the invention are not limited to these.

1. 3-Hydroxy-6-methylpyridazine



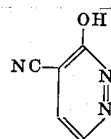
2. 3-Hydroxypyridazine



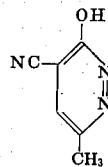
3. 3-Hydroxy-6-carboxypyridazine



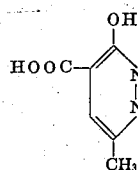
4. 3-Hydroxy-4-cyanopyridazine



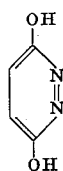
5. 3-Hydroxy-4-cyano-6-methylpyridazine



6. 3-Hydroxy-4-carboxy-6-methylpyridazine

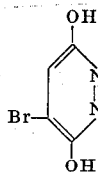


7. 3,6-Dihydroxypyridazine

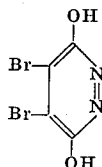


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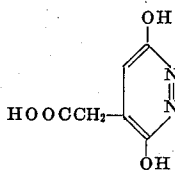
8. 3,6-Dihydroxy-4-bromopyridazine



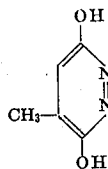
9. 3,6-Dihydroxy-4,5-dibromopyridazine



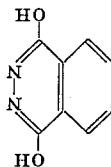
10. 3,6-Dihydroxy-4-carboxymethylpyridazine



11. 3,6-Dihydroxy-4-methylpyridazine

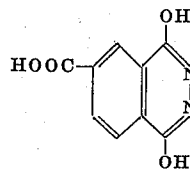


12. 1,4-Dihydroxyphthalazine



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13. 1,4-Dihydroxy-6-carboxy-phthalazine



The developer formulation according to the present invention is markedly excellent in preservability and does not injure the photographic property of the resulting linear or dot image.

The present invention is illustrated below with reference to an example.

EXAMPLE

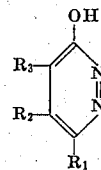
A commercially available lithographic film was exposed to light through a gray-scale, and was then developed at 27°C. for 2 minutes with each of the developers of the composition shown below immediately after preparation and the same developers as above except that these had been incubated for 24 hours in contact with the air (contact area 28 cm²/liter). Thereafter, the sample was subjected to fixing, water-washing and drying treatments and measured in photographic properties to obtain the results as set forth in the table shown below.

| Compound | Amount (g/l) | Relative speed | Gamma |
|---------------------------|-------------------|-------------------------------|-------|
| Exemplified compound (1) | 4 | Immediately after preparation | 25 |
| | | After 24 hours' incubation | 23 |
| Exemplified compound (7) | 3 | Immediately after preparation | 24 |
| | | After 24 hours' incubation | 22 |
| Exemplified compound (11) | 5 | Immediately after preparation | 24 |
| | | After 24 hours' incubation | 21 |
| Exemplified compound (12) | 3 | Immediately after preparation | 25 |
| | | After 24 hours' incubation | 23 |
| Control developer | No compound added | Immediately after preparation | 22 |
| | | After 24 hours' incubation | 15 |

As is clear from the above table, the developer compositions according to the present invention are extremely lower in degradation of infectious developability due to contact with the air, and hence can give images sufficiently satisfactory in photographic properties.

What we claim is:

1. A developer composition of low free sulfite concentration for silver halide-containing lithographic printing plates which comprises an infectious developer containing hydroquinone as developing agent and, incorporated therein, a compound of the formula,



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wherein R₁ is a hydrogen atom, a lower alkyl group, a hydroxy group or a carboxy group; R₂ is a hydrogen atom, a lower alkyl group, a halogen atom or a carboxy-lower alkyl group; and R₃ is a hydrogen atom, a cyano group, a halogen atom or a carboxy group, provided that R₂ and R₃ may bond together to form a benzene ring.

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2. A developer composition as claimed in claim 1, wherein said compound is selected from the group consisting of 3-hydroxy-6-methylpyridazine, 3,6-dihydroxypyridazine, 3,6-dihydroxy-4-methylpyridazine and 1,4-dihydroxyphthalazine.

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