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PATENT SPECIFICATION

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(54) PHOTORESIST COMPOSITION

(71) We, HITACHI LTD., a corporation organised under the laws of Japan, of 5-1, 1-chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a photoresist composition comprising a water-soluble polymer and a bis-azide cross linking agent.

It is known that photo-sensitive composition comprising a bis-azide cross linking agent and a water-soluble polymer such as polyvinyl alcohol, polyacrylamide, polyvinyl pyrrolidone or gelatine have previously been used as a material for forming an image. In these compositions, the azide groups of the bis-azide cross linking agent are decomposed by exposure to ultraviolet light. On decomposition, the water-soluble polymer present becomes cross linked. In this way, the water-soluble polymer is converted into a water-insoluble polymer and so a latent image is formed.

However, this cross linking is influenced by the extent of decomposition of the bis-azide cross linking agent, which in turn depends on the degree of exposure to ultraviolet rays. A problem with existing photo-sensitive materials of this type is that a latent image cannot be formed satisfactorily with a limited exposure to ultraviolet rays, in other words, the material has low sensitivity.

The present invention is concerned with improving the sensitivity of such compositions.

The present invention provides a photoresist composition comprising a water-soluble polymer, a bis-azide photo-cross linking agent, and a water-soluble aliphatic alcohol having 4 to 6 carbon atoms and 4 to 6 hydroxyl groups. The water-soluble alcohol is preferably added in an amount of 1 to 100 parts by weight, and more preferably 5 to 50 parts by weight, per 100 parts by weight of the water-soluble polymer.

The water-soluble polymers which may be used in the compositions according to the present invention include polyvinyl pyrrolidone, polyacrylamide, polyvinyl alcohol, gelatine, acrylamide - N - [2 - (2 - methyl - 4 - oxopentyl)] - acrylamide copolymer, acrylamide-vinyl alcohol copolymer, acrylamide-vinylpyrrolidone copolymer or mixtures thereof. The bis-azide cross linking agent may be sodium 4,4' - diazidostilbene - 2,2' - disulphonate, sodium 4,4' - diazidobenzalacetophenone - 2 - sulphonate or sodium 4,4' - diazidostilbene - α - carboxylate.

The aliphatic alcohols which may be used in the composition include erythritols ($C_4H_8(OH)_4$), pentitols ($C_5H_{10}(OH)_5$) such as arabitol or xylitol, or hexitols ($C_6H_{12}(OH)_6$) such as sorbitol, dulcitol or mannitol.

The polyhydric aliphatic alcohol in the compositions of this invention accelerates polymer cross linking. It is therefore possible for polymer cross linking to occur to form a latent image even with a low exposure to ultraviolet rays.

The compositions of the invention may include an agent such as vinyltris (β -methoxyethoxy) silane, N - β - (aminoethyl) - γ - aminopropylmethoxysilane or N - β - (aminoethyl) - γ - aminopropyltrimethoxysilane, to improve the adhesiveness of the composition to a substrate.

The present invention also includes a method of forming an image which comprises exposing a composition according to the invention to ultraviolet light through an image and developing the resulting latent image by removal of non-cross-linked composition.

The following Examples, in which all parts are expressed by weight, unless otherwise indicated, illustrate the invention.

EXAMPLE 1

Four sensitive compositions were prepared by adding 0, 0.10, 0.25 and 0.5 part of sorbitol ($C_6H_{12}(OH)_6$), respectively, to a photo-sensitive material (photoresist) prepared by dissolving in 100 parts of water 1 part of polyvinyl pyrrolidone as the water-soluble polymer and 0.2 part of sodium 4,4' - diazidostilbene - 2,2' - disulphonate. Each composition was coated onto glass and dried. The resulting photo-sensitive layer was exposed to

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ultraviolet rays stepwise by the use of an optical wedge and was then subjected to development with warm water. This development removed those portions of the layer where the exposure was insufficient to cause cross linking. The least exposed portions formed in the respective four layers were compared to calculate the relative exposures of these portions. The results obtained are as follows:

Amount of sorbitol added (parts)	Relative exposure
0	1
0.10	0.85
0.25	0.7
0.5	0.5

As is clear from the above data, the photo-sensitivity was improved by the addition of sorbitol.

Similar results were obtained by replacing sorbitol by dulcitol or mannitol.

EXAMPLE 2

Four sensitive compositions were prepared by adding 0, 0.10, 0.25 and 0.5 part of arabitol ($C_6H_7(OH)_5$), respectively, to a photo-sensitive material prepared by dissolving in 100 parts of water a mixture of 0.5 part of polyvinyl pyrrolidone and 0.5 part of polyacrylamide as the water-soluble polymers, 0.3 part of sodium 4,4' - diazidostilbene - 2,2' - disulphonate as a photo-cross linking agent and 0.01 part of an alkoxysilane to improve adhesion to the glass. Each composition was subjected to the same treatment as described in Example 1. The results obtained are as follows:

Amount of arabitol added (parts)	Relative exposure
0	1
0.10	0.9
0.25	0.85
0.5	0.7

Similar results were obtained by replacing arabitol by xylitol. These results show that

photo-sensitivity was improved by incorporating the aliphatic alcohol.

WHAT WE CLAIM IS:—

1. A photoresist composition comprising a water-soluble polymer, a bis-azide photo-cross linking agent, and a water-soluble aliphatic alcohol having 4 to 6 carbon atoms and 4 to 6 hydroxyl groups.

2. A composition according to claim 1, wherein the amount of said alcohol is 1 to 100 parts by weight per 100 parts by weight of said water-soluble polymer.

3. A composition according to claim 1 or 2, wherein said alcohol is an erythritol, a pentitol or a hexitol.

4. A composition according to any one of the preceding claims, wherein said water-soluble polymer is polyvinyl pyrrolidone, polyacrylamide, polyvinyl alcohol, gelatine, acrylamide - N - [2 - (2 - methyl - 4 - oxopentyl)] - acrylamide copolymer, acrylamide-vinyl alcohol copolymer, acrylamide-vinylpyrrolidone copolymer or mixtures thereof.

5. A composition according to any one of the preceding claims, wherein said bis-azide is sodium 4,4' - diazidostilbene - 2,2' - disulphonate, sodium 4,4' - diazidobenzalacetophenone - 2 - sulphonate or sodium 4,4' - diazidostilbene - α - carboxylate.

6. A composition according to any one of the preceding claims which contains an agent which increases the adhesiveness of the composition to a substrate.

7. A composition according to claim 1, substantially as hereinbefore described with reference to any one of the Examples.

8. A method of forming an image which comprises exposing a composition according to any one of the preceding claims to ultraviolet light through an image and developing the resulting latent image by removal of non-cross-linked compositions.

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2. A composition according to claim 1, wherein the amount of said alcohol is 1 to 100 parts by weight per 100 parts by weight of said water-soluble polymer.

3. A composition according to claim 1 or 2, wherein said alcohol is an erythritol, a pentitol or a hexitol.

4. A composition according to any one of the preceding claims, wherein said water-soluble polymer is polyvinyl pyrrolidone, polyacrylamide, polyvinyl alcohol, gelatine, acrylamide - N - [2 - (2 - methyl - 4 - oxopentyl)] - acrylamide copolymer, acrylamide-vinyl alcohol copolymer, acrylamide-vinylpyrrolidone copolymer or mixtures thereof.

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