

PATENT SPECIFICATION

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(54) PHOTORESIST COMPOSITION

(71) We, HITACHI LTD., a Japanese body corporate 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 which can prevent coating unevenness or drying unevenness in the formation of a photoresist layer.

Photoresists comprising a water-soluble polymer and a bis-azide photo-crosslinking agent have heretofore been used widely in photographic printing or photo-etching. For this purpose, it is necessary to form a photoresist layer on the surface of a base plate or a member to be etched; this is generally carried out by a rotational coating method. The photoresist layer is capable of directly forming an image and its sensitivity varies remarkably according to the difference in film thickness and drying degree after coating. Such a photoresist layer should therefore have a uniform film thickness and be dried uniformly to obtain an even image of a high precision.

In the previously known methods for the formation of a photoresist layer, the rate of revolution in rotational photoresist coating methods or the drying temperature is fixed at an appropriate value taking into account the viscosity of the photoresist or the surface state of a material to be coated. However, the prior art photoresist suffers from the defect that it is difficult to determine the above-mentioned appropriate values and a uniform coating film is difficult to obtain, particularly when the base plate has a large area or a special shape, since drying is comparatively rapidly finished and the fluidity of the photoresist is poor.

The present invention is based on the discovery that a photoresist layer having a uniform film thickness can be produced by increasing the fluidity of the photoresist and moderately

retarding drying and that this can be achieved by using a photoresist composition containing a low molecular weight dihydric alcohol.

More specifically, the present invention provides a photoresist composition comprising a water-soluble polymer, a bis-azide photo-crosslinking agent and a dihydric aliphatic alcohol having a molecular weight less than 134.18.

The amount of the alcohol is preferably 5 to 300 parts by weight, especially 20 to 200 parts by weight, per 100 parts by weight of the water-soluble polymer. If the amount of alcohol added is less than the above-mentioned values, the desired effect cannot be obtained, while if the amount added is more than the above-mentioned values, the sensitivity or resolving power is reduced.

Examples of water-soluble polymer which may be used in the present invention include gelatine, homopolymers such as polyacrylamide, polyvinyl pyrrolidone, polyvinyl methyl ether and polyvinyl acetal, and copolymers such as acrylamide - N - [2 - (2 - methyl-4 - oxopentyl)] - acrylamide copolymer, acrylamide-vinyl methyl ether copolymer, maleic acid-vinyl methyl ether copolymer and acrylamide-vinylpyrrolidone copolymer. Examples of suitable bis-azide photo-crosslinking agents are 4,4' - diazidostilbene - 2,2' - disulfonic acid, 4,4' - diazidostilbene - α - carboxylic acid and metal salts thereof.

The alcohol is preferably water-soluble, is compatible with the water-soluble polymer, is in the form of a liquid at ordinary temperature and has a boiling point higher than that of water which means that it is difficult to evaporate. Examples of such alcohols are ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,3-butyleneglycol and 1,5-pentanediol. If the molecular weight of these alcohols is too high, the fluidity of the photoresist becomes poor and coating film-uniformizing effect is reduced. For this reason, the alcohols preferably have a molecular weight of 60 to 110.

Alcohol	Molecular weight	Melting point (°C)	Boiling point (°C)
Ethylene glycol	62.07	-12.6	197.7 - 197.8
Diethylene glycol	106.12	-11.5	245.0
Propylene glycol	76.10	-59	187.3
Dipropylene glycol	134.18	-	233
1,3-Butylene glycol	90.12	-77	207.5
1,5-Pentane-diol	104.15	-18	239 - 240

If desired, compounds which improve the adhesion of the photoresist to the support, such as vinyltris - (β - methoxyethoxy)silane, N - β - (aminoethyl) - γ - aminopropylmethyltrimethoxysilane or N - β - (aminoethyl) - γ - aminopropyltrimethoxysilane can be added to the photoresist.

The photoresist compositions of the present invention are solutions which are difficult to evaporate and their fluidity is increased by a reduction in their viscosity. On coating of the photoresists, therefore, a uniform coating film can be easily obtained irrespective of the shape of the base plate to be coated or the coating area and the influence of the rate of revolution in rotational coating is reduced. Further, on drying of the photoresists, drying is retarded and thereby it is possible to prevent drying unevenness caused by a change in drying temperature or heating unevenness and form a photoresist layer having a uniform film thickness.

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

Example 1.

Two photoresist liquids were prepared by dissolving one part of polyacrylamide as a water-soluble polymer and 0.2 part of sodium 4,4' - diazidostilbene - 2,2' - disulfonate as a bis - azide crosslinking agent in 100 parts of water and then adding 0.2 part of ethylene glycol to one of the solutions. Each photoresist liquid was dropped onto a 200 mm $\times$ 150 mm glass base plate, rotation-coated at 150 r.p.m. and dried by a 100 W infrared heater for 5 minutes to form a photoresist layer. An optical mask, in which round holes

of 0.4 mm in diameter were two-dimensionally arranged at a pitch of 0.65 mm, was placed at a distance of about 1 cm from the photoresist layer. Exposure was carried out with a point source of light and development was then carried out by a water spray (water pressure 1 kg/cm²). When the respective images thus obtained were observed, it was found that the image formed with the photoresist containing ethylene glycol produced no unevenness in contrast with the image formed with photoresist containing no ethylene glycol.

Example 2.

Two photoresists were prepared by dissolving a water-soluble polymer consisting of 0.5 part of polyvinyl pyrrolidone and 0.5 part of polyacrylamide, 0.4 part of sodium 4,4' - diazidostilbene - 2,2' - disulfonate as a bis-azide crosslinking agent and 0.05 part of N - β - (aminomethyl) - γ - aminopropyltrimethoxysilane as an adhesiveness improver in 100 parts of water and then adding 0.5 part of propylene glycol to one of the solutions. Each photoresist was coated onto the inner surface of the front panel of a 20-inch color television receiver by a rotational coater and then dried by an infrared heater provided with ten 200 W lamps on the whole of one side for 3 minutes, drying having been finished at a panel temperature of 45°C. Ultraviolet rays were irradiated through a shadow mask, in which holes of 0.34 mm in diameter were two-dimensionally arranged at a pitch of 0.65 mm, at an illuminance of 1500 luxes for two minutes, and development was carried out by a water spray (water pressure 1 kg/cm²). As a result, the photoresist containing propylene

glycol produced no unevenness in image in contrast with the photoresist containing no propylene glycol. Also, the unevenness produced in the photoresist containing no propylene glycol caused a difference in the size of the formed dot image; this is believed to be the result of a difference in sensitivity caused by nonuniformity in the film thickness of photoresist or the drying degree of film.

Example 3.

Two photoresists were prepared by dissolving a mixture of 1.5 parts of polyvinyl pyrrolidone and 1 part of gelatine as water-soluble polymers 0.3 part of sodium 4,4' - diazido-stilbene - 2,2' - disulfonate as a bis-azide crosslinking agent, and 0.02 part of N- β -(aminoethyl) - γ - aminopropylmethyldimethoxysilane as an adhesiveness improver in 100 parts of water and then adding 2 parts of 1,3-butylene glycol to one of the solutions. Each photoresist was subjected to the same experiment as described in Example 2. It was found that the image produced with the photoresist containing the alcohol produced no unevenness.

WHAT WE CLAIM IS:—

1. A photoresist composition comprising a water-soluble polymer, a bis-azide photocrosslinking agent and a dihydric aliphatic alcohol having a molecular weight less than 134,18.
2. A photoresist composition according to claim 1, wherein the amount of said alcohol is 5 to 300 parts by weight per 100 parts by weight of the water-soluble polymer.
3. A photoresist composition according to claim 1 or 2 wherein said alcohol has a molecular weight of 60 to 110.
4. A photoresist composition according to claim 1 or 2 wherein said alcohol is ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,3-butylene glycol or 1,5-pentanediol.
5. A photoresist composition according to

any one of the preceding claims wherein said water-soluble polymer is gelatine, polyacrylamide, polyvinyl pyrrolidone, polyvinyl methyl ether, polyvinyl acetal, an acrylamide-N-[2-(2-methyl-4-oxopentyl)]acrylamide copolymer, an acrylamide-vinyl alcohol copolymer, an acrylamide-vinylpyrrolidone copolymer or a maleic acid-vinyl methyl ether copolymer.

6. A photoresist composition according to any one of the preceding claims in which the water-soluble polymer is a mixture of polyacrylamide and polyvinyl pyrrolidone, or an acrylamide N - [2 - (2 - methyl - 4 - oxopentyl)]acrylamide copolymer.

7. A photoresist composition according to any one of the preceding claims wherein said bis-azide photocrosslinking agent is 4,4'-diazido-stilbene-2,2'-disulfonic acid, or 4,4'-diazidostilbene - α - carboxylic acid or a metal salt thereof.

8. A photoresist composition according to any one of the preceding claims which further contains a compound which improves the adhesion of the photoresist to a support.

9. A process for preparing a plate for use in photographic printing or photo-etching, which process comprises coating a composition as claimed in any one of the preceding claims on the surface of a base plate.

10. A process according to claim 9 substantially as hereinbefore described.

11. A plate obtained by a process as claimed in claim 9 or 10.

12. A process for preparing a printing plate, which process comprises imagewise exposing a plate as claimed in claim 11 to actinic radiation and removing unexposed portions of photoresist.

13. A printing plate obtained by a process as claimed in claim 12.

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4. A photoresist composition according to claim 1 or 2 wherein said alcohol is ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, 1,3-butylene glycol or 1,5-pentanediol.
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any one of the preceding claims wherein said water-soluble polymer is gelatine, polyacrylamide, polyvinyl pyrrolidone, polyvinyl methyl ether, polyvinyl acetal, an acrylamide-N-[2-(2-methyl-4-oxopentyl)]acrylamide copolymer, an acrylamide-vinyl alcohol copolymer, an acrylamide-vinylpyrrolidone copolymer or a maleic acid-vinyl methyl ether copolymer.

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7. A photoresist composition according to any one of the preceding claims wherein said bis-azide photo-crosslinking agent is 4,4'-diazido-stilbene-2,2'-disulfonic acid, or 4,4'-diazidostilbene - α - carboxylic acid or a metal salt thereof.

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