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(71) Applicant: **Fujifilm Corporation**
Minato-ku
Tokyo 106-8620 (JP)

(72) Inventors:
- **Takanashi, Genki**
  Shizuoka 421-0396 (JP)
- **Oohashi, Hidekazu**
  Shizuoka 421-0396 (JP)

(74) Representative: **HOFFMANN EITLE**
Patent- und Rechtsanwälte
Arabellastrasse 4
81925 München (DE)

(54) Fountain solution composition for lithographic printing

(57) [Problems to be Solved] A fountain solution composition for lithographic printing, which is superior in preventing dirt at a non-image area of a lithographic plate, is provided. Especially, provided is a fountain solution composition for lithographic printing, which can attain high quality printing by mitigating dirt after a break caused by dirt at a non-image area of a plate at a restart of printing after a stop of a printing press, and further by suppressing decrease in the ink density at an image area, even when the component concentration of the fountain solution is increased.

[Solution] A fountain solution composition for lithographic printing characterized by comprising a star polymer having at least one hydrophilic group; the fountain solution composition for lithographic printing, wherein the star polymer is a star polymer having 3 branches to 10 branches; the fountain solution composition for lithographic printing, wherein 3 branches to 10 branches of polymer chains are branched from a skeleton through sulfide bonds in the star polymer.; the fountain solution composition for lithographic printing, wherein the star polymer is a polymer having 3 branches to 10 branches of polymer chains branched from a skeleton through sulfide bonds, the polymer being obtained by polymerizing an ethylenic unsaturated monomer in the presence of a multifunctional thiol; the fountain solution composition for lithographic printing, wherein the star polymer further comprises at least one substrate adsorptive group; and the fountain solution composition for lithographic printing as a concentrated fountain solution composition.

EP 2 543 518 A2

Description

[Technical Field]

[0001] The present invention relates to a fountain solution composition for lithographic printing, and more specifically to a fountain solution composition for lithographic printing to be used for an offset printing process.

[Background Art]

[0002] Lithography is a printing process utilizing the nature that water and oil do not mix each other inherently. The surface of a printing plate is composed of a non-image area, which receives water and repels oil based ink, and an image area, which repels water and receives oil based ink. By wetting a non-image area with a fountain solution, the surface chemical difference with an image area is enlarged, and the ink repellency of a non-image area and the ink receptivity of an image area are intensified.
A lithographic press is usually based on an offset printing process, in which an ink and a fountain solution are supplied on to a plate, the ink attaches to an image area and the fountain solution attaches to a non-image area to form an image, and the image on the plate is transferred to a rubber blanket, and is further transferred from the rubber blanket to a paper to complete printing.

[0003] Conventionally, as a fountain solution, an aqueous solution containing a colloidal substance, such as a bichromate, a phosphate, gum arabic, and carboxymethylcellulose (CMC), has been known. There have been drawbacks in it, however, that a non-image area of a plate cannot be dampened uniformly by containing only such a compound which may give a smudged print out, and the control of the supply quantity of the fountain solution requires considerable skills. To mitigate such drawbacks, the Dahlgren system, in which an aqueous solution containing approx. 20 to 25% of isopropyl alcohol is used as a fountain solution, has been proposed. However, since isopropyl alcohol is volatile, it requires special equipment to maintain constant its concentration in the fountain solution. Further, isopropyl alcohol has an unpleasant odor, and is not preferable from a standpoint of the work environment.

[0004] As a fountain solution without containing isopropyl alcohol have been proposed recently a fountain solution containing a specific propylene glycol series compound (see Patent Literature 1); a fountain solution containing an addition compound of ethylenediamine with ethylene oxide and propylene oxide (see Patent Literature 2 and 3); and a fountain solution containing an addition compound of diethylenetriamine with ethylene oxide and propylene oxide (see Patent Literature 4). Further, as printing chemicals to be used in a fountain solution, etc., in Patent Literature 5 are described printing chemicals containing a water soluble polymer having an adsorptive group, which can be adsorbed on the surface of a plate substrate for lithographic printing, and a sulfonic acid group. Patent Literature 6 proposes addition of a diol series compound to overcome a drawback of such (so-called) blanket piling that an ink component and a paper component build up gradually at a non-image area on a rubber blanket over long-time continuous printing.
While, as a problem during a lithography printing process there is a pending problem that dirt appears on a non-image area, more specifically, when a printing press is stopped for a while for some reasons such as a tea break, at restart of printing a tiny speck may occasionally appear at a non-image area (hereinafter referred to as "dirt after a break"). Consequently, it is desirous to prevent dirt at a non-image area and minimize the paper consumed for cleaning in starting printing by lithography (at the initial start of printing) or at a restart.
For preventing dirt at a non-image area it is conceivable to increase the additive concentration of a fountain solution, but if the fountain solution concentration is increased, the water quantity to an image area increase to lower the ink density leading to deterioration of the print quality as the result.

[Citation List]

[Patent Literature]

[0005]

[Patent Literature 1] Japanese Published Unexamined Application No. 2001-138655;
[Patent Literature 2] Japanese Published Unexamined Application No. 2007-50665;
[Patent Literature 3] Japanese Published Unexamined Application No. 2007-168124;
[Patent Literature 4] Japanese Published Unexamined Application No. 2007-55182;
[Patent Literature 5] Japanese Published Unexamined Application No. 2007-38483; and
[Patent Literature 6] Japanese Published Unexamined Application No. 2009-234247.

[Summary of Invention]

[Technical Problem]

[0006] A means for preventing as much as possible appearance of dirt on a plate surface at a non-image area, which has heretofore constituted drawbacks, and a means for providing efficiently a high quality print by mitigating inconveniences to be caused by such dirt on a plate surface at a non-image area, have been asked for. It is conceivable to devise such means from a viewpoint of a fountain solution composition.
An object of the present invention is to provide a fountain solution composition for lithographic printing which is superior in preventing dirt at a non-image area of a lithographic plate. Another object of the present invention is to provide a fountain solution composition for lithographic printing, which can attain effectively high quality printing by mitigating dirt at a non-image area during the initial startup of printing, or dirt after a break, caused by dirt at a non-image area of a plate surface at a restart of printing after a stop of a printing press.
An additional object of the present invention is to provide a fountain solution composition for lithographic printing, which can suppress decrease in the ink density at an image area attaining high quality printing, even when the component concentration of the fountain solution is increased.

[Solution to Problem]

[0007] The present inventors studied intensively to discover that by adding a specific polymer into a fountain solution composition for lithographic printing the objects can be accomplished thereby completing the present invention.
Consequently, the present invention is a fountain solution composition for lithographic printing characterized by containing a star polymer having at least one hydrophilic group.
As the star polymer one containing further at least one substrate adsorptive group is also preferable.

[0008] As the star polymer, a star polymer having 3 branches to 10 branches (both inclusive) can be favorably used. As for a specific structure of a star polymer, it has 3 branches to 10 branches (both inclusive) of polymer chains branched from a skeleton through sulfide bonds, and more specifically it has 3 branches to 10 branches (both inclusive) of polymer chains branched from a skeleton through sulfide bonds, the polymer being obtained by polymerizing an ethylenic unsaturated monomer in the presence of a multifunctional thiol.

[0009] Examples of at least one hydrophilic group in a star polymer of the present invention include at least one selected from the group consisting of a sulfonic acid group and a salt thereof, an amide group, a polyalkylene oxide group, a hydroxy group, a sulfuric monoester group and a salt thereof, a sulfonamide group, an amino group, a sulfuric acid-monoamide group and a salt thereof, and a betaine structure.
Examples of a substrate adsorptive group of a star polymer include at least one selected from the group consisting of a phosphonic acid group and a salt thereof, a phosphoric ester group and a salt thereof, and a carboxylic acid group and a salt thereof.

[0010] Examples of a preferable embodiment of the present invention include a fountain solution composition for lithographic printing containing a water soluble polymer not having a star structure.
Examples of the water soluble polymer not having a star structure include at least one water soluble macromolecular compound selected from the group consisting of gum arabic, a cellulose derivative and a modification thereof, polyvinyl alcohol and a derivative thereof, polyvinylpyrrolidone, a vinyl methyl ether/maleic anhydride copolymer, a vinyl acetate/maleic anhydride copolymer, a styrene/maleic anhydride copolymer, a water soluble soybean polysaccharides, starch, a starch derivative, pullulan and a pullulan derivative, gelatin, and hemicellulose extracted from a soybean.
The present invention is directed also to a fountain solution composition for lithographic printing as a concentrated fountain solution composition having the above described characteristics.

[Advantageous Effects of Invention]

[0011] A fountain solution composition for lithographic printing according to the present invention is superior in prevention of dirt at a non-image area of a lithographic plate.
With a fountain solution composition for lithographic printing according to the present invention a high quality print can be provided effectively by mitigating dirt after a break, which is caused by dirt at a non-image area at a restart of printing after a stop of a printing press. More particularly, with a fountain solution composition for lithographic printing according to the present invention a printing operation can be conducted with limited number of waste of paper. The term "waste of paper" or "waste paper" means herein the number of paper sheets required from the start of printing until an ink disappears completely from a non-image area on a print out. With a fountain solution composition for lithographic printing according to the present invention a good print out can be provided with little paper waste at a restart of printing, after a printing press is stopped during a printing operation.

Further, if the concentration of an additive, etc. in a fountain solution is increased in order to prevent dirt at a non-image area, decrease in the ink density at an image area can be prevented, and as the result a high quality print can be provided.

[Description of Embodiments]

[0012] The components of a fountain solution composition for lithographic printing according to the present invention will be described below.

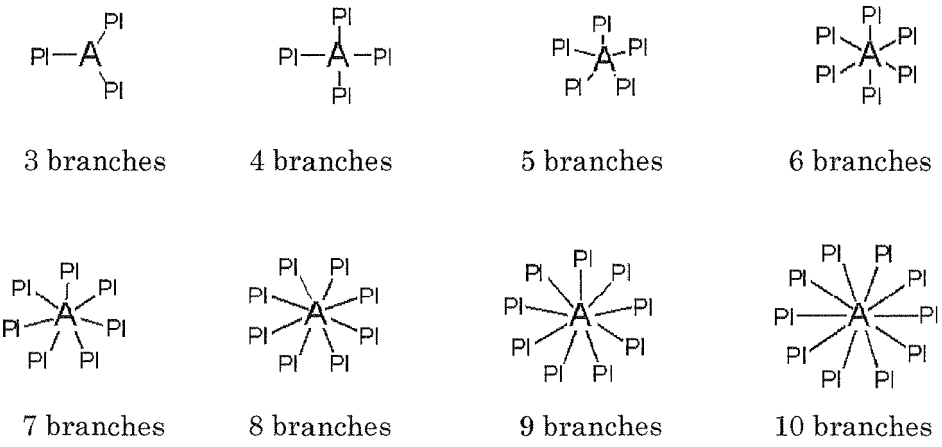
[I] Star polymer

[0013] A star polymer to be used according to the present invention is a kind of a branched macromolecule, namely a polymer having a structure, in which 3 or more linear macromolecules bond especially at a single point.

[0014] Examples of the structure of a star polymer to be used according to the present invention are schematically shown with a skeleton A and polymer chains Pl as follows. Namely, it has a structure in which either of the terminals of a plurality of polymer chains Pl bond to the skeleton A, and an appropriate branch number is 3 to 10.

[0015]

FIG. 1

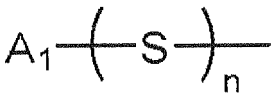


[0016] Any star polymer may be used as a star polymer to be used according to the present invention, insofar as it has the structure depicted above.

Examples of such a star polymer include a star polymer prepared by a coupling process or a living anion process as described in "Shin Jikken-kagaku Kouza, Koubunshi Kagaku I", edited by The Chemical Society of Japan, p. 208 to 210; a star polymer prepared by a synthetic method conducting a polymerization reaction under photoirradiation using as an initiator a compound containing a dithiocarbamate group and/or a compound containing a xanthate group as described in Japanese Published Unexamined Application No. 10-279867; and a star polymer prepared by a usual radical polymerization using a multifunctional thiol as a chain transfer agent.

[0017] As a star polymer according to the present invention, from viewpoints of the easiness in synthesis and the performance of an obtained polymer, a polymer prepared by polymerizing an ethylenic unsaturated monomer in the presence of a multifunctional thiol, constituted of polymer chains branched from a skeleton through sulfide bonds is preferable. Namely, one having a hub portion, which is a 3 or more functional thiol residue as the skeleton, is preferable. In an idealized structure, a main chain of an addition polymer outshoots from each thio part in the hub. Consequently, 3 or more main chains outshoot from thio parts. Namely, a skeleton A preferably has a structure represented by the following general formula (1).

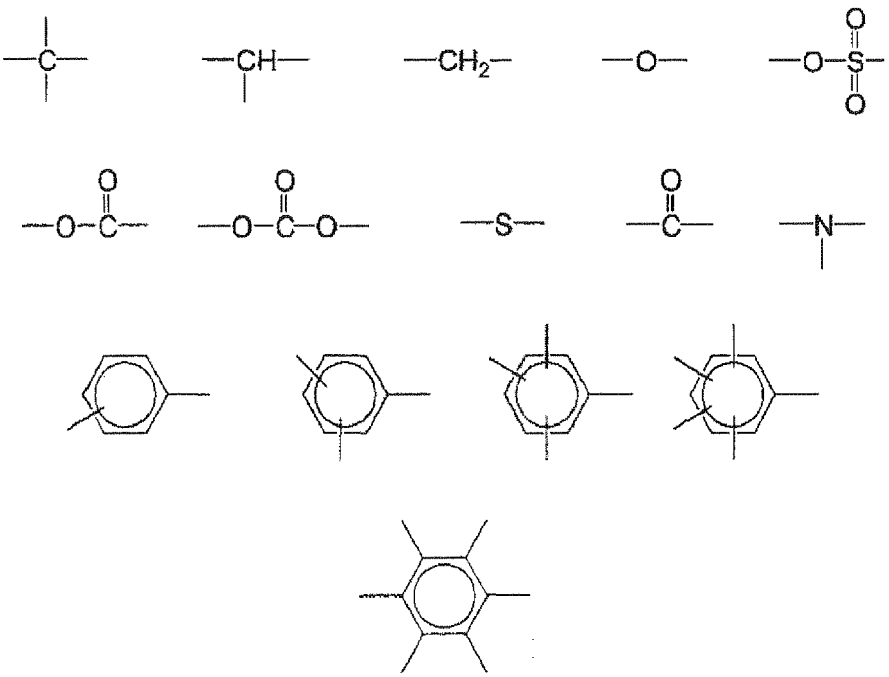
[0018]



General formula (1)

wherein A_1 is an n-valent organic group, and n is an integer of 3 or higher. Specific examples of A_1 include the following structures and an organic group constituted to n-valent by a combination of a plurality of the following structures. Preferably, n is an integer of 3 to 10, more preferably an integer of 3 to 8, and especially preferably an integer of 4 to 8.

[0019]



— CH_3 Multivalent naphthalene, Multivalent anthracene

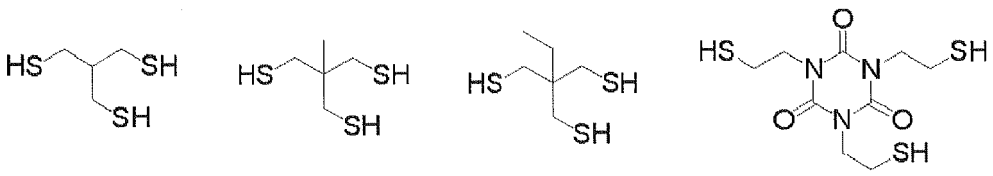
(Skelton of polymer with polymer chains branched through sulfide bonds)

[0020] Although as a multifunctional thiol to be used in a synthesis of a star polymer according to the present invention, any compound having a plurality of thiol groups per each molecule can be favorable used, a multifunctional thiol with 3 to 10 functional groups is preferable, a thiol with 3 to 8 functional groups is more preferable, and a thiol with 4 to 8 functional groups is especially preferable.

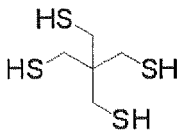
[0021] Examples of such a multifunctional thiol include the following compound A to compound F.

(Compound A)

[0022] Compound A is a compound prepared by reacting an electrophile, such as a halogenide, and a sulfonic acid ester with an alcohol, with a sulfurizing agent, such as thiourea, potassium thiocyanate, and thioacetic acid, followed by various treatments. Specific examples of the compound A include the following compounds, but the present invention is not limited thereto.



(SA-1) (SA-2) (SA-3) (SA-4)



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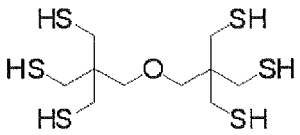
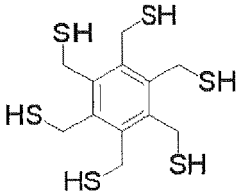
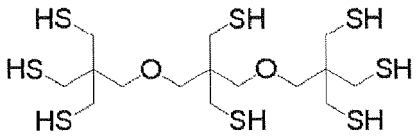


(SA-6)



(SA-7)



(SA-8)

(Compound B)

[0023] A compound B is a compound prepared by a dehydration condensation reaction between a multifunctional alcohol and a carboxylic acid having a thiol group, and among others a compound prepared by a condensation reaction between a multifunctional alcohol with 3 to 10 functional groups and a monocarboxylic acid with a single thiol group is preferable.

[0024] Specific examples of a multifunctional alcohol include cyclohexanetriol (3), glycerol (3), 2-hydroxymethyl-1,3-propanediol (3), 1,1,1-tris(hydroxymethyl)ethane (3), 1,2,4-butanetriol (3), trimethylol propane (3), 1,2,3-trihydroxyhexane (3), 1,2,6-trihydroxyhexane (3), 1,2,3-heptanetriol (3), pyrogallol (3), 1,2,4-benzenetriol (3), phloroglucinol (3), 1,1,1-tris(4-hydroxyphenyl)ethane (3), 1,3,5-tris(2-hydroxyethyl)isocyanurate (3), pentaerythritol (4), threitol (4), erythritol (4), xylulose (4), ribulose (4), quebrachitol (5), adonitol (5), arabitol (5), xylitol (5), catechin (5), epicatechin (5), inositol (6), sorbitol (6), mannitol (6), iditol (6), dulcitol (6), dipentaerythritol (6), and tripentaerythritol (8). While, a numeral in ( ) means a number of functional groups.

[0025] Among the multifunctional alcohols, cyclohexanetriol, glycerol (3), 2-hydroxymethyl-1,3-propanediol (3), 1,1,1-tris(hydroxymethyl)ethane (3), trimethylol propane (3), phloroglucinol (3), 1,1,1-tris(4-hydroxyphenyl)ethane (3), 1,3,5-tris(2-hydroxyethyl)isocyanurate (3), pentaerythritol (4), catechin (5), epicatechin (5), inositol (6), dipentaerythritol (6), and tripentaerythritol (8) are preferable; cyclohexanetriol (3), 2-hydroxymethyl-1,3-propanediol (3), 1,1,1-tris(hydroxymethyl)ethane (3), trimethylol propane (3), phloroglucinol (3), 1,1,1-tris(4-hydroxyphenyl)ethane (3), 1,3,5-tris(2-hydroxyethyl)isocyanurate (3), pentaerythritol (4), catechin (5), epicatechin (5), inositol (6), dipentaerythritol (6), and tripentaerythritol (8) are more preferable; and 1,3,5-tris(2-hydroxyethyl)isocyanurate (3), pentaerythritol (4), catechin (5), epicatechin (5), inositol (6), dipentaerythritol (6), and tripentaerythritol (8) are especially preferable. While, a numeral in ( ) means a number of functional groups.

[0026] Specific examples of a monocarboxylic acid having a thiol group include mercaptoacetic acid, 3-mercaptopropionic acid, 2-mercaptopropionic acid, 3-mercapto isobutyric acid, *N*-acetylcysteine, *N*-(2-mercaptopropionyl)glycine, and thiosalicylic acid.

Mercaptoacetic acid, 3-mercaptopropionic acid, 2-mercaptopropionic acid, 3-mercapto isobutyric acid, *N*-acetylcysteine, and *N*-(2-mercaptopropionyl)glycine are preferable; 3-mercaptopropionic acid, 2-mercaptopropionic acid, 3-mercapto isobutyric acid, *N*-acetylcysteine, and *N*-(2-mercaptopropionyl)glycine are more preferable; and 3-mercaptopropionic acid, 3-mercapto isobutyric acid, *N*-acetylcysteine, and *N*-(2-mercaptopropionyl)glycine are especially preferable.

Specific examples of a compound B include the following compounds, provided that it is not limited thereto.

[0027]

[Table 1]

Multifunctional alcohol	Carboxylic acid having thiol group						
	mercapto-acetic acid	3-mercapto-propionic acid	2-mercapto-propionic acid	3-mercapto-isobutyric acid	N-acetyl-cysteine	N-(2-mercaptopropiony 1) glycine	thiosalicylic acid
cyclohexanetriol (3)	SB-1	SB-2	SB-3	SB-4	SB-5	SB-6	SB-7
glycerol (3)	SB-8	SB-9	SB-10	SB-11	SB-12	SS-13	SB-14
2-hydroxymethy-1, 3-propanediol(3)	SB-15	SB-16	SB-17	SB-18	SB-19	SB-20	SB-21
1,1,1-tris (hydroxymethyl) ethane (3)	SB-22	SB-23	SB-24	SB-25	SB-26	SB-27	SB-28
1,2,4-butanetriol (3)	SB-29	SB-30	SB-31	SB-32	SB-33	SB-34	SB-35
trimethylolpropane (3)	SB-36	SB-37	SB-38	SB-39	SB-40	SB-41	SB-42
1,2,3-trihydroxyex ane (3)	SB-43	SB-44	SB-45	SB-46	SB-47	SB-48	SB-49
1,2,6-trihydroxyex ane (3)	SB-50	SB-51	SB-52	SB-53	SB-54	SB-55	SB-56
1,2,3-heptanetriol (3)	SB-57	SB-58	SB-59	SB-60	SB-61	SB-62	SB-63
pyrogallol (3)	SB-64	SB-65	SB-66	SB-67	SB-68	SB-69	SB-70
1,2,4-benzenetriol (3)	SB-71	SB-72	SB-73	SB-74	SB-75	SB-76	SB-77
phloroglucinol (3)	SB-78	SB-79	SB-80	SB-81	SB-82	SB-83	SB-84
1,1,1-tris (4-hydroxyphenyl)e thane (3)	SB-85	SB-86	SB-87	SB-88	SB-89	SB-90	SB-91
1,3,5-tris (2-hydroxyethyl)iso cyanurate (3)	SB-92	SB-93	SB-94	SB-95	SB-96	SB-97	SB-98
pentaerythritol (4)	SB-99	SB-100	SB-101	SB-102	SB-103	SB-104	SB-105
threitol(4)	SB-106	SB-107	SB-108	SB-109	SB-110	SB-111	SB-112
erythritol (4)	SB-113	SB-114	SB-115	SB-116	SB-117	SB-118	SB-119
xylulose (4)	SB-120	SB-121	SB-122	SB-123	SB-124	SB-125	SB-126
quebrachitol (5)	SB-127	SB-128	SB-129	SB-130	SB-131	SB-132	SB-133
adonitol (5)	SB-134	SB-135	SB-136	SB-137	SB-138	SB-139	SB-140
arabitol (5)	SB-141	SB-142	SB-143	SB-144	SB-145	SB-146	SB-147
xylitol (5)	SB-148	SB-149	SB-150	SB-151	SB-152	SB-153	SB-154
catechin (5)	SB-155	SB-156	SB-157	SB-158	SB-159	SB-160	SB-161
epicatechin (5)	SB-162	SB-163	SB-164	SB-165	SB-166	SB-167	SB-168
inositol (6)	SB-169	SB-170	SB-171	SB-172	SS-173	SB-174	SB-175

(continued)

Multifunctional alcohol	Carboxylic acid having thiol group						
	mercapto-acetic acid	3-mercapto-propionic acid	2-mercapto-propionic acid	3-mercapto-isobutyric acid	N-acetyl-cysteine	N-(2-mercaptopropiony 1) glycine	thiosalicylic acid
sorbitol (6)	SB-176	SB-177	SB-178	SB-179	SB-180	SB-181	SB-182
mannitol (6)	SB-183	SB-184	SB-185	SB-186	SB-187	SB-188	SB-189
iditol (6)	SB-190	SB-191	SB-192	SB-193	SB-194	SB-195	SB-196
dulcitol (6)	SB-197	SB-198	SB-199	SB-200	SB-201	SB-202	SB-203
dipentaerythritol (6)	SB-204	SB-205	SB-206	SB-207	SB-208	SB-209	SB-210
tripentaerythritol (8)	SB-211	SB-212	SB-213	SB-214	SB-215	SB-216	SB-217

[0028] Among the specific examples in Table 1 are preferable SB-1 to SB-34, SB-36 to SB-48, SB-50 to SB-55, SB-57 to SB-62, SB-64 to SB-69, SB-71 to SB-76, SB-78 to SB-111, SB-113 to SB-118, SB-120 to SB-125, SB-127 to SB-132, SB-134 to SB-139, SB-141 to SB-146, SB-148 to SB-153, SB-155 to SB-181, SB-183 to SB-188, SB-190 to SB-195, SB-197 to SB-202, and SB-204 to SB-217; more preferable are SB-1 to SB-6, SB-9 to SB-13, SB-15 to SB-20, SB-22 to SB-27, SB-36 to SB-41, SB-78 to SB-83, SB-85 to SB-90, SB-92 to SB-97, SB-99 to SB-104, SB-155 to SB-160, SB-162 to SB-167, SB-169 to SB-174, SB-204 to SB-209, and SB-211 to SB-216; especially preferable are SB-2 to SB-6, SB-16 to SB-20, SB-23 to SB-27, SB-37 to SB-41, SB-79 to SB-83, SB-86 to SB-90, SB-93 to SB-97, SB-100 to SB-104, SB-156 to SB-160, SB-163 to SB-167, SB-170 to SB-174, SB-205 to SB-209, and SB-212 to SB-216.
Since the distances among the thiol groups in the above multifunctional thiol are long, the steric hindrance is limited allowing building a desired star structure.

(Compound C)

[0029] A compound C is a compound prepared by a dehydration condensation reaction between a multifunctional amine and a carboxylic acid having a thiol group, and among others a compound prepared by a condensation reaction between a multifunctional amine with 3 to 10 functional groups and a monocarboxylic acid with a thiol group is preferable.
[0030] Specific examples of a multifunctional amine include diethylenetriamine (3), *N*-(2-aminoethyl)-1,3-propanediamine (3), *N*-(3-aminopropyl)-1,3-propanediamine (3), spermidine (3), bis(hexamethylene)triamine (3), 4-(aminomethyl)-1,8-octanediamine (3), triethylenetetramine (4), 1,4,7,11-tetraazaundecane (4), *N,N*'-bis(3-aminopropyl)ethylenediamine (4), *N,N*'-bis(2-aminoethyl)-1,3-propanediamine (4), *N,N*'-bis(3-aminopropyl)-1,3-propanediamine (4), spermine (4), tris(2-aminoethyl)amine (3), tetraethylenepentamine (5), pentaethylenehexamine (6), 1,4,7-triazacyclononane (3), 1,5,9-triazacyclododecane (3), cyclene (4), 1,4,8,11-tetraazacyclotetradecane (4), 1,4,8,12-tetraazacyclopentadecane (4), hexacyclene (6), 3,3'-diaminobenzidine (4), and 1,2,4,5-benzenetetramine (4). While, a numeral in ( ) means a number of functional groups.
[0031] Among the multifunctional amines are preferable 4-(aminomethyl)-1,8-octanediamine (3), triethylenetetramine (4), 1,4,7,11-tetraazaundecane (4), *N,N*'-bis(3-aminopropyl)ethylenediamine (4), *N,N*'-bis(2-aminoethyl)-1,3-propanediamine (4), *N,N*'-bis(3-aminopropyl)-1,3-propanediamine (4), spermine (4), tris(2-aminoethyl)amine (3), tetraethylenepentamine (5), pentaethylenehexamine (6), cyclene (4), and hexacyclene (6); more preferable are 4-(aminomethyl)-1,8-octanediamine (3), tris(2-aminoethyl)amine (3), tetraethylenepentamine (5), pentaethylenehexamine (6), cyclene (4), and hexacyclene (6); and especially preferable are tetraethylenepentamine (5), pentaethylenehexamine (6), cyclene (4), and hexacyclene (6).
[0032] Specific examples of the carboxylic acid having a thiol group include the carboxylic acids described for the compound B. Specific examples of the compound include the following compounds, provided that the present invention is not limited thereto.
[0033]

[Table 2]

Multifunctional alcohol	Carboxylic acid having thiol group						
	mercapto-acetic acid	3-mercapto-propionic acid	2-mercapto-propionic acid	3-mercapto-isobutyric acid	N-acetyl-cysteine	N-(2-mercaptopropiony 1) glycine	thiosalicylic acid
diethylenetriamine (3)	SC-1	SC-2	SC-3	SC-4	SC-5	SC-6	SC-7
N-(2-aminoethyl)-1, 3-propanediamine (3)	SC-8	SC-9	SC-10	SC-11	SC-12	SC-13	SC-14
N-(3-aminopropyl)-1,3-propaned_iamine (3)	SC-15	SC-16	SC-17	SC-18	SC-19	SC-20	SC-21
spennidine (3)	SC-22	SC-23	SC-24	SC-25	SC-26	SC-27	SC-28
bis(hexamethylene) triamine (3)	SC-29	SC-30	SC-31	SC-32	SC-33	SC-34	SC-35
4-(aminomethyl)-1, 8-octanediamine (3)	SC-36	SC-37	SC-38	SC-39	SC-40	SC-41	SC-42
triethylenetetramine (4)	SC-43	SC-44	SC-45	SC-46	SC-47	SC-48	SC-49
1,4,7,11-tetraazaund ecane (4)	SC-50	SC-51	SC-52	SC-53	SC-54	SC-55	SC-56
N,N'-bis(3-aminopropyl) ethylenediamine (4)	SC-57	SC-58	SC-59	SC-60	SC-61	SC-62	SC-63
N,N'-bis(2-aminoethyl)-1,3-propanediamine (4)	SC-64	SC-65	SC-66	SC-67	SC-68	SC-69	SC-70
N,N'-bis(3-aminopropyl)-1,3-propanediamine (4)	SC-71	SC-72	SC-73	SC-74	SC-75	SC-76	SC-77
spermine (4)	SC-78	SC-79	SC-80	SC-81	SC-82	SC-83	SC-84
tris(2-aminoethyl)amine (3)	SC-85	SC-86	SC-87	SC-88	SC-89	SC-90	SC-91
tetraethylenepentamine (5)	SC-92	SC-93	SC-94	SC-95	SC-96	SC-97	SC-98
pentaethylenehexamine (6)	SC-99	SC-100	SC-101	SC-102	SC-103	SC-104	SC-105
1,4,7-triazacyclononane (3)	SC-106	SC-107	SC-108	SC-109	SC-110	SC-111	SC-112

(continued)

Multifunctional alcohol	Carboxylic acid having thiol group						
	mercapto-acetic acid	3-mercapto-propionic acid	2-mercapto-propionic acid	3-mercapto-isobutyric acid	N-acetyl-cysteine	N-(2-mercaptopropiony 1) glycine	thiosalicylic acid
1,5,9-triazacyclododecane (3)	SC-113	SC-114	SC-115	SC-116	SC-117	SC-118	SC-119
cyclen (4)	SC-120	SC-121	SC-122	SC-123	SC-124	SC-125	SC-126
1,4,8,11-tetraazacyclotetradecane (4)	SC-127	SC-128	SC-129	SC-130	SC-131	SC-132	SC-133
1,4,8,12-tetraazacyclopentadecane (4)	SC-134	SC-135	SC-136	SC-137	SC-138	SC-139	SC-140
hexacyclen (6)	SC-141	SC-142	SC-143	SC-144	SC-145	SC-146	SC-147

[0034] Among the specific examples in Table 2 are preferable SC-1 to SC-6, SC-8 to SC-13, SC-15 to SC-20, SC-22 to SC-27, SC-29 to SC-34, SC-36 to SC-111, SC-113 to SC-118, SC-120 to SC-132, SC-134 to SC-139, and SC-141 to SC-147; more preferable are SC-37 to SC-41, SC-44 to SC-48, SC-51 to SC-55, SC-58 to SC-62, SC-65 to SC-69, SC-72 to SC-76, SC-79 to SC-83, SC-86 to SC-90, SC-93 to SC-97, SC-100 to SC-104, SC-121 to SC-125, and SC-142 to SC-146; and especially preferable are SC-37 to SC-41, SC-86 to SC-90, SC-93 to SC-97, SC-100 to SC-104, SC-121 to SC-125, and SC-142 to SC-146.
Since the distances among the thiol groups in the above multifunctional thiol are long, the steric hindrance is limited allowing building a desired star structure.

(Compound D)

[0035] A compound D is a compound prepared by a dehydration condensation reaction between a compound having alcohol and amine and a carboxylic acid having a thiol group, and a compound prepared by a condensation reaction between a multifunctional alcoholamine with 3 to 10 functional groups of alcohol and amine and a monocarboxylic acid with a thiol group is preferable.

[0036] Specific examples of a multifunction alcoholamine include diethanolamine (3), serinol (3), diisopropanolamine (3), 2-amino-2-ethyl-1,3-propanediol (3), 2-amino-2-methyl-1,3-propanediol (3), tris(hydroxymethyl)aminomethane (4), bishomoTRIS (4), 1,3-diamino-2-hydroxypropane (3), 2-(2-aminoethylamino)ethanol (3), *N,N'*-bis(2-hydroxyethyl)ethylenediamine (4), 1,3-bis[tris(hydroxymethyl)methylamino]propane (8), 1-amino-1-deoxy-D-sorbitol (6), *N*-methyl-D-glucamine (6), 2,3-diaminophenol (3), 4-aminoresorcinol (3), norphenylephrine (3), octopamine (3), synephrine (3), 3,4-dihydroxybenzylamine (3), 3-hydroxytyramine (3), norepinephrine (4), 5-hydroxydopamine (4), and 6-hydroxydopamine (4); serinol (3), 2-amino-2-methyl-1,3-propanediol (3), tris(hydroxymethyl)aminomethane (4), bishomoTRIS (4), 1,3-diamino-2-hydroxypropane (3), N,N'-bis(2-hydroxyethyl)ethylenediamine (4), 1,3-bis[tris(hydroxymethyl)methylamino]propane (8), 1-amino-1-deoxy-D-sorbitol (6), *N*-methyl-D-glucamine (6), norepinephrine (4), 5-hydroxydopamine (4), and 6-hydroxydopamine (4) are preferable; and tris(hydroxymethyl)aminomethane (4), bishomotris (4), *N,N*'-bis(2-hydroxyethyl)ethylenediamine (4), 1,3-bis[tris(hydroxymethyl)methylamino]propane (8), 1-amino-1-deoxy-D-sorbitol (6), *N*-methyl-D-glucamine (6), norepinephrine (4), 5-hydroxydopamine (4), and 6-hydroxydopamine (4) are especially preferable. While, a numeral in ( ) means a number of functional groups.
Specific examples of the carboxylic acid having a thiol group include the carboxylic acids described for the compound B. Specific examples of the compound include the following compounds, provided that the present invention is not limited thereto.

[0037]

[Table 3]

Multifunctional alcohol	Carboxylic acid having thiol group						
	mercapto-acetic acid	3-mercapto-propionic acid	2-mercapto-propionic acid	3-mercapto-isobutyric acid	N-acetyl-cysteine	N-(2-mercaptopropiony 1) glycine	thiosalicylic acid
diethanolamine (3)	SD-1	SD-2	SD-3	SD-4	SD-5	SD-6	SD-7
serinol (3)	SD-8	SD-9	SD-10	SD-11	SD-12	SD-13	SD-14
diisopropanolamine (3)	SD-15	SD-16	SD-17	SD-18	SD-19	SD-20	SD-21
2-amino-2-ethyl-1,3 -propanediol (3)	SD-22	SD-23	SD-24	SD-25	SD-26	SD-27	SD-28
2-amino-2-methyl-1 ,3-propanediol (3)	SD-29	SD-30	SD-31	SD-32	SD-33	SD-34	SD-35
tris(hydroxymethyl) aminomethane (4)	SD-36	SD-37	SD-38	SD-39	SD-40	SD-41	SD-42
bis-homotris (4)	SD-43	SD-44	SD-45	SD-46	SD-47	SD-48	SD-49
1,3-diamino-2-hydroxypropane (3)	SD-50	SD-51	SD-52	SD-53	SD-54	SD-55	SD-56
2-(2-aminoethylami no) ethanol (3)	SD-57	SD-58	SD-59	SD-60	SD-61	SD-62	SD-63
N,N'-bis(2-hydroxy ethyl) ethylenediamine (4)	SD-64	SD-65	SD-66	SD-67	SD-68	SD-69	SD-70
1,3-bis[tris(hydroxy methyl) methylamino]propane (8)	SD-71	SD-72	SD-73	SD-74	SD-75	SD-76	SD-77
1-aminol-1-deoxy-D-sorbitol (6)	SD-78	SD-79	SD-80	SD-81	SD-82	SD-83	SD-84
N-methylD-glucamine (6)	SD-85	SD-86	SD-87	SD-88	SD-89	SD-90	SD-91
2,3-diaminophenol (3)	SD-92	SD-93	SD-94	SD-95	SD-96	SD-97	SD-98
4-aminoresorcinol (3)	SD-99	SD-100	SD-101	SD-102	SD-103	SD-104	SD-105
norphenylephrine (3)	SD-106	SD-107	SD-108	SD-109	SD-110	SD-111	SD-112

(continued)

Multifunctional alcohol	Carboxylic acid having thiol group						
	mercapto-acetic acid	3-mercapto-propionic acid	2-mercapto-propionic acid	3-mercapto-isobutyric acid	N-acetyl-cysteine	N-(2-mercaptopropiony 1) glycine	thiosalicylic acid
octopamine (3)	SD-113	SD-114	SD-115	SD-116	SD-117	SD-118	SD-119
synephrine (3)	SD-120	SD-121	SD-122	SD-123	SD-124	SD-125	SD-126
3,4-dihydroxybenzylamine (3)	SD-127	SD-128	SD-129	SD-130	SD-131	SD-132	SD-133
3-hydroxytyramine (3)	SD-134	SD-135	SD-136	SD-137	SD-138	SD-139	SD-140
norepinephrine(4)	SD-141	SD-142	SD-143	SD-144	SD-145	SD-146	SD-147
5-hydroxydopamine (4)	SD-148	SD-149	SD-150	SD-151	SD-152	SD-153	SD-154
6-hydroxydopamine (4)	SD-155	SD-156	SD-157	SD-158	SD-159	SD-160	SD-161

[0038] Among the specific examples in Table 3 are preferable SD-1 to SD-6, SD-8 to SD-20, SD-22 to SD-27, SD-29 to SD-62, SD-64 to SD-97, SD-99 to SD-104, SD-106 to SD-111, SD-113 to SD-118, SD-120 to SD-125, SD-127 to SD-132, SD-134 to SD-139, and SD-141 to SD-161; more preferable are SD-9 to SD-13, SD-30 to SD-34, SD-37 to SD-41, SD-44 to SD-48, SD-51 to SD-55, SD-65 to SD-69, SD-72 to SD-76, SD-79 to SD-83, SD-86 to SD-90, SD-142 to SD-146, SD-149 to SD-153, and SD-156 to SD-160; and especially preferable are SD-37 to SD-41, SD-44 to SD-48, SD-65 to SD-69, SD-72 to SD-76, SD-79 to SD-83, SD-86 to SD-90, SD-142 to SD-146, SD-149 to SD-153, and SD-156 to SD-160.
Since the distances among the thiol groups in the above multifunctional thiol are long, the steric hindrance is limited allowing building a desired star structure.

(Compound E)

[0039] A compound E is a compound prepared by a dehydration condensation reaction between a multifunctional carboxylic acid and an alcohol having a thiol group, and among others a compound prepared by a condensation reaction between a multifunctional carboxylic acid with 2 to 10 functional groups and an alcohol with 1 or more thiol groups is preferable.

[0040] Specific examples of a multifunctional carboxylic acid include oxalic acid (2), malonic acid (2), methylmalonic acid (2), succinic acid (2), methylsuccinic acid (2), glutaric acid (2), adipic acid (2), pimelic acid (2), suberic acid (2), azelaic acid (2), sebacic acid (2), tricarballylic acid (3), 1,2,3,4-butanetetracarboxylic acid (4), aconitic acid (3), hexafluoroglutaric acid (2), malic acid (2), tartaric acid (2), citric acid (3), diglycolic acid (2), 3,6-dioxaoctanedicarboxylic acid (2), tetrahydrofuran-2,3,4,5-tetracarboxylic acid (4), mercaptosuccinic acid (2), thiodiglycolic acid (2), 2,2',2",2"'-[1,2-ethanediylidenetetrakis(thio)]tetrakisacetic acid (4), 1,3,5-cyclohexanetricarboxylic acid (3), 1,2,3,4-cyclobutanetetracarboxylic acid (4), 1,2,3,4,5,6-cyclohexanehexacarboxylic acid (6), 1,2-phenylenediacetic acid (2), 1,2-phenylenedioxydiacetic acide (2), homophthalic acid (2), 1,3-phenylenediacetic acid (2), 4-carboxyphenoxyacetic acid (2), 1,4-phenylenediacetic acid (2), 1,4-phenylenedipropionic acid e (2), phthalic acid (2), isophthalic acid (2), terephthalic acid (2), 1,2,3-benzenetricarboxylic acid (3), 1,2,4-benzenetricarboxylic acid (3), 1,3,5-benzenetricarboxylic acid (3), 1,2,4,5-benzenetetracarboxylic acid (4), melissic acid (6), and 1,4,5,8-naphthalenetetracarboxylic acid (4); preferable are tricarballylic acid (3), 1,2,3,4-butanetetracarboxylic acid (4), aconitic acid (3), citric acid (3), tetrahydrofuran-2,3,4,5-tetracarboxylic acid (4), mercaptosuccinic acid (2), 2,2',2",2'"-[1,2-ethanediylidenetetrakis(thio)]tetrakisacetic acid (4), 1,3,5-cyclohexanetricarboxylic acid (3), 1,2,3,4-cyclobutanetetracarboxylic acid (4), 1,2,3,4,5,6-cyclohexanehexacarboxylic acid (6), 1,2-phenylenediacetic acid (2), 1,2-phenylenedioxydiacetic acid (2), 1,3-phenylenediacetic acid (2), 1,4-phenylenediacetic acid (2), 1,4-phenylenedipropionic acid (2), phthalic acid (2), isophthalic acid (2), terephthalic acid (2), 1,3,5-benzenetricarboxylic acid (3), 1,2,4,5-benzenetetracarboxylic acid (4), melissic acid (6), and 1,4,5,8-naphthalenetetracarboxylic acid (4); and especially preferable are tricarballylic (3), 1,2,3,4-butanetetracarboxylic acid (4), tetrahydrofuran-2,3,4,5-tetracarboxylic acid (4), mercaptosuccinic acid (2), 2,2',2",2'"-[1,2-ethanediylidenetetrakis(thio)]tetrakisacetic acid (4), 1,3,5-cyclohexanetricarboxylic acid (3), 1,2,3,4-cyclobutanetetracarboxylic acid (4), 1,2,3,4,5,6-cyclohexanehexacarboxylic acid (6), 1,3,5-benzenetricarboxylic acid (3), 1,2,4,5-benzenetetracarboxylic acid (4), melissic acid (6), and 1,4,5,8-naphthalenetetracarboxylic acid (4). While, a numeral in ( ) means a number of functional groups.

[0041] Specific examples of an alcohol having a thiol group include 2-mercaptoethanol (1), 1-mereapto-2-propanol (1), 3-mercapto-1-propanol (1), 3-mercapto-2-butanol (1), 2,3-dimercapto-1-propanol (2), and 4-hydroxythiophenol (1); preferable are 2-mercaptoethanol (1), 3-mercapto-1-propanol (1), and 2,3-dimercapto-1-propanol (2); more preferable are 2-mercaptoethanol (1), and 3-mercapto-1-propanol (1); and especially preferable is 3-mercapto-1-propanol (1). A numeral in ( ) means a number of functional groups.
Examples of the compound include the compounds listed in Table 4 and Table 5 below, provided that it is not limited thereto.

[0042]

[Table 4]

Multifunctional alcohol	Alcohol having thiol group					
	2-mercapto-ethanol	1-mercapto-2-propanol	3-mercapto-1-propanol	3-mercapto-2-butanol	2,3-dimercaptol-propanol	4-hydroxythiophenol
oxalic acid (2)					SE-1	
malonic acid (2)					SE-2	
methylmalonic acid (2)					SE-3	
succinic acid (2)					SE-4	
methylsuccinic acid (2)					SE-5	
glutaric acid (2)					SE-6	

adipic acid (2)					SE-7	
pimelic acid (2)					SE-8	
suberic acid (2)					SE-9	
azelaic acid (2)					SE-10	
sebacic acid (2)					SE-11	
tricarballylic acid (3)	SE-12	SE-13	SE-14	SE-15	SE-16	SE-17
1,2,3,4-butanetetracarboxylic acid (4)	SE-18	SE-19	SE-20	SE-21	SE-22	SE-23
aconitic acid (3)	SE-24	SE-25	SE-26	SE-27	SE-28	SE-29
hexafluoroglutaric acid (2)					SE-30	
marinic acid (2)					SE-31	
tartaric acid (2)					SE-32	
citric acid (3)	SE-33	SE-34	SE-35	SE-36	SE-37	SE-38
diglycolic acid (2)					SE-39	
3,6-dioxaoctanedicarboxylic acid (2)					SE-40	
tetrahydrofuran-2,3,4,5-tetracarboxylic acid (4)	SE-41	SE-42	SE-43	SE-44	SE-45	SE-46
mercaptosuccinic acid (2)	SE-119	SE-120	SE-121	SE-122	SE-47	SE-123
thiodiglycolic acid (2)					SE-48	
2,2',2",2"'-[1,2-ethanediylidenetetrakis(thio)]tetrakisacetic acid (4)	SE-49	SE-50	SE-51	SE-52	SE-53	SE-54

[0043] [Table 5]

Multifunctional	Alcohol having thiol group

alcohol	2-mercapto-ethanol	1-mercapto-2-propanol	3-mercapto-1-propanol	3-mercapto-2-butanol	2,3-dimercapto1-propanol	4-hydroxythiophenol
1,3,5-cyclohexanetricarboxylic acid (3)	SE-55	SE-56	SE-57	SE-58	SE-59	SE-60
1,2,3,4-cyclobutanetetracarboxylic acid (4)	SE-61	SE-62	SE-63	SE-64	SE-65	SE-66
1,2,3,4,5,6-cyclohexanehexacarboxylic acid (6)	SE-67	SE-68	SE-69	SE-70	SE-71	SE-72
1,2-phenylenediacetic acid (2)					SE-73	
1,2-phenylenedioxydiacetic acid (2)					SE-74	
homophthalic acid (2)					SE-75	
1,3-phenylenediacetic acid (2)					SE-76	
4-carboxyphenoxyacetic acid (2)					SE-77	
1,4-phenylenediacetic acid (2)					SE-78	
1,4-phenylenedipropionic acid (2)					SE-79	
phthalic acid (2)					SE-80	
isophthalic acid (2)					SE-81	
terephthalic acid (2)					SE-82	
1,2,3-benzenetricarboxylic acid (3)	SE-83	SE-84	SE-85	SE-86	SE-87	SE-88
1,2,4-benzenetricarboxylic acid (3)	SE-89	SE-90	SE-91	SE-92	SE-93	SE-94

1,3,5-benzenetricarboxylic acid (3)	SE-95	SE-96	SE-97	SE-98	SE-99	SE-100
1,2,4,5-benzenetetracarboxylic acid (4)	SE-101	SE-102	SE-103	SE-104	SE-105	SE-106
mellitilic acid (6)	SE-107	SE-108	SE-109	SE-110	SE-111	SE-112
1,4,5,8-naphthalenetetracarboxylic acid (4)	SE-113	SE-114	SE-115	SE-116	SE-117	SE-118

[0044] Among those listed in Tables 4 and 5 are preferable SE-12, SE-14, SE-16, SE-18, SE-20, SE-22, SE-24, SE-26, SE-33, SE-35, SE-41, SE-43, SE-45, SE-119, SE-121, SE-47, SE-49, SE-51, SE-53, SE-55, SE-57, SE-59, SE-61, SE-63, SE-65, SE-67, SE-69, SE-71, SE-83, SE-85, SE-89, SE-91, SE-95, SE-97, SE-99, SE-101, SE-103, SE-105, SE-107, SE-109, SE-111, SE-113, SE-115, and SE-117; and more preferable are SE-12, SE-14, SE-18, SE-20, SE-41, SE-43, SE-119, SE-121, SE-49, SE-51, SE-55, SE-57, SE-61, SE-63, SE-67, SE-69, SE-95, SE-97, SE-101, SE-103, SE-107, SE-109, SE-113, and SE-115.
Since the distances among the thiol groups in the above multifunctional thiol are long, the steric hindrance is limited allowing building a desired star structure.

(Compound F)

[0045] A compound F is a compound prepared by a dehydration condensation reaction between a multifunctional carboxylic acid and an amine having a thiol group, and among others a compound prepared by a condensation reaction between a multifunctional carboxylic acid with 2 to 10 functional groups and an amine with 1 or more thiol groups is preferable.
Specific examples of a multifunctional carboxylic acid include the above described multifunctional carboxylic acids. Specific examples of an amine with 1 or more thiol groups include 2-aminoethanethiol, 2-aminothiophenol, 3-aminothiophenol, and 4-aminothiophenol; preferable are 2-aminoethanethiol, and 4-aminothiophenol; and more preferable is 2-aminoethanethiol.
Specific examples of the compound include the following compounds, provided that the present invention is not limited thereto.
[0046]

[Table 6]

Multifunctional carboxylic acid	Amine having thiol group			
	2-amino-ethanethiol	2-amino-thiophenol	3-amino-thiophenol	4-amino-thiophenol
tricarballylic acid(3)	SF-1	SF-2	SF-3	SF-4
1,2,3,4-butanetetracarboxylic acid(4)	SF-5	SF-6	SF-7	SF-8
aconitic acid(3)	SF-9	SF-10	SF-11	SF-12
citric acid(3)	SF-13	SF-14	SF-15	SF-16
tetrahydrofuran-2,3,4,5-tetracarboxylic acid(4)	SF-17	SF-18	SF-19	SF-20
mercaptosuccinic acid(2)	SF-21	SF-22	SF-23	SF-24
2,2',2",2'"-[1,2-ethanediylid enetetrakis(thio)] tetrakisace tic acid(4)	SF-25	SF-26	SF-27	SF-28

(continued)

Multifunctional carboxylic acid	Amine having thiol group			
	2-amino-ethanethiol	2-amino-thiophenol	3-amino-thiophenol	4-amino-thiophenol
1,3,5-cyclohexanetricarboxylic acid(3)	SF-29	SF-30	SF-31	SF-32
1,2,3,4-cyclobutanetetracarboxylic acid(4)	SF-33	SF-34	SF-35	SF-36
1,2,3,4,5,6-cyclohexanehexacarboxylic acid(6)	SF-37	SF-38	SF-39	SF-40
1,2,3-benzenetricarboxylic acid(3)	SF-41	SF-42	SF-43	SF-44
1,2,4-benzenetricarboxylic acid(3)	SF-45	SF-46	SF-47	SF-48
1,3,5-benzenetricarboxylic acid(3)	SF-49	SF-50	SF-51	SF-52
1,2,4,5-benzenetetracarboxylic acid(4)	SF-53	SF-54	SF-55	SF-56
mellitilic acid(6)	SF-57	SF-58	SF-59	SF-60
1,4,5,8-naphthalenetetracarboxylic acid(4)	SF-61	SF-62	SF-63	SF-64

[0047] Among those listed in Tables 6 are preferable SF-1, SF-4, SF-5, SF-8, SF-9, SF-13, SF-17, SF-20, SF-21, SF-24, SF-25, SF-28, SF-29, SF-32, SF-33, SF-36, SF-37, SF-40, SF-41, SF-45, SF-49, SF-52, SF-53, SF-56, SF-57, SF-60, SF-61, and SF-64; and more preferable are SF-1, SF-5, SF-17, SF-21, SF-25, SF-29, SF-33, SF-37, SF-49, SF-53, SF-57, and SF-61.
Since the distances among the thiol groups in the above multifunctional thiol are long, the steric hindrance is limited allowing building a desired star structure.

[0048] Among the multifunctional thiols, from viewpoints of plate life and development property, the compound A to the compound E are preferable, the compound A, the compound B, the compound C, and the compound E are more preferable, and the compound A, the compound B, and the compound C are especially preferable.

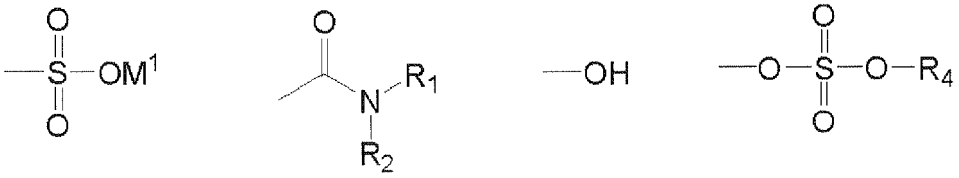
[Polymer chain]

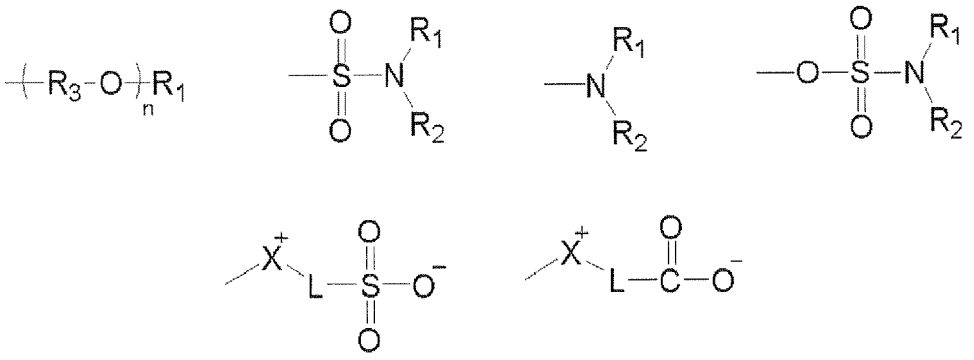
[0049] Examples of a polymer chain in a star polymer to be used according to the present invention include a vinyl polymer, a (meth)acrylic acid series polymer, and a styrene series polymer, which have been heretofore known and can be produced by a radical polymerization; and a (meth)acrylic acid series polymer is especially preferable.

(Hydrophilic group)

[0050] A star polymer to be used according to the present invention has at least one hydrophilic group. A polymer chain of a star polymer to be used according to the present invention has at least one hydrophilic group in order to enhance the hydrophilicity of the surface of a substrate and improve the resistance to dirt. More preferably a star polymer having at least one hydrophilic group contains a recurring unit having at least one hydrophilic group as a copolymer component. A polymer chain of a star polymer to be used according to the present invention may have one, or two or more such hydrophilic groups.

[0051] Specific examples of the hydrophilic group include the following.



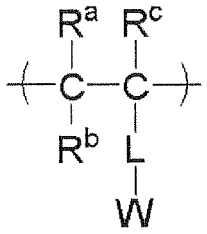


[0052] In the formulas, M^1 represents a hydrogen atom, a metal atom belonging to an alkali metal or an alkaline earth metal, or an ammonium group. X^+ is a group expressed by $-N^+R_1R_2-$, $-S^+R_1-$, $-I^+-$, and $-P^+R_1R_2-$. R_1, R_2 independently represent a hydrogen atom, an alkyl group, an aryl group, an alkenyl group, and alkynyl group; R_3 represents an alkylene group; and R_4 represents a hydrogen atom, an alkyl group, an aryl group, an alkenyl group, and an alkynyl group. The n represents an integer of 1 to 100. L has the same meaning as defined for the formula (B1) described below.
More specifically, R_1 is preferably a hydrogen atom or a C1 to C3 alkyl group, and among others preferably a hydrogen atom or a methyl group. R_2 is preferably a hydrogen atom or a C1 to C3 alkyl group, and among others preferably a hydrogen atom or a methyl group. R_3 is preferably a C2 to C5 alkylene group, and among others preferably ethylene or propylene. R_4 is preferably a hydrogen atom or a C1 to C6 alkyl group, and the n is preferably an integer of 2 to 90.

[0053] Although any functional group, which can enhance the affinity with water, can be utilized favorably as a hydrophilic group; and a sulfonic acid (salt) group, an amide group, a polyalkylene oxide group, a hydroxy group, a sulfuric monoester (salt) group, a sulfonamide group, an amino group, a sulfuric monoamide (salt) group, and a betaine structure are preferable; a sulfonic acid (salt) group, an amide group, a polyalkylene oxide group, a hydroxy group, a sulfuric monoester (salt) group, a sulfonamide group, an amino group, a sulfuric monoamide (salt) group, and a betaine structure are more preferable, and a sulfonic acid (salt) group, an amide group, a polyalkylene oxide group, a hydroxy group and a betaine structure are especially preferable.

[0054] Specific examples of a recurring unit having a hydrophilic group according to the present invention are preferably expressed by the following general formula (B2).

[0055]

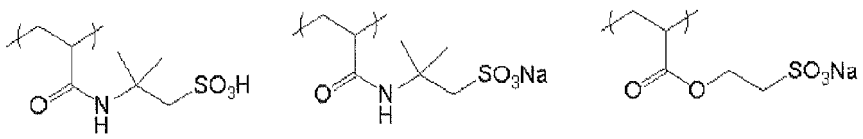


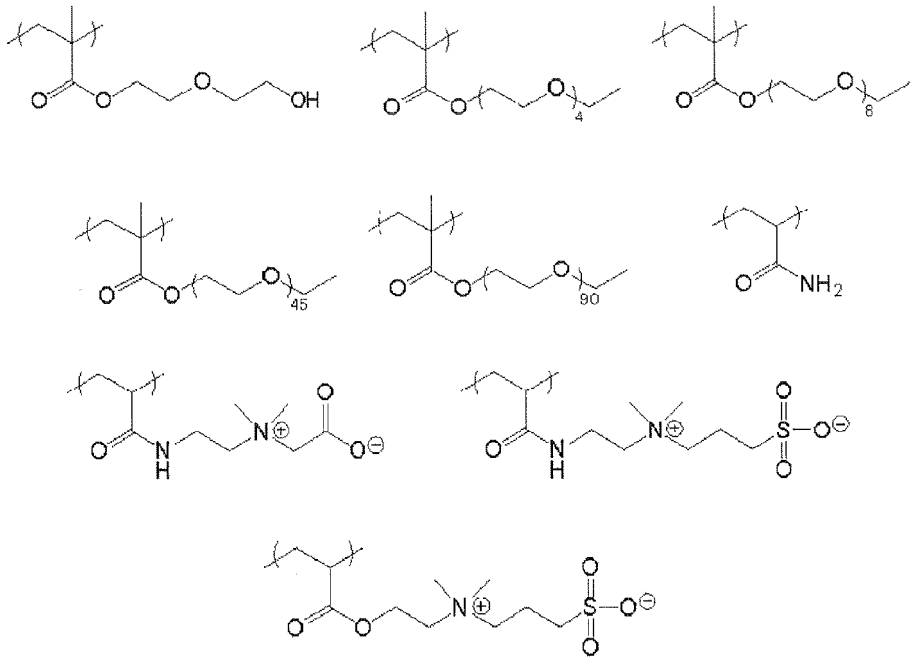
(B2)

[0056] In the formula, R^a to R^c independently represent a hydrogen atom, a C1 to C6 alkyl group, or a halogen atom. L has the same meaning as described above. W represents a hydrophilic group and preferable embodiments are as described above.

[0057] Specific examples of a recurring unit having a hydrophilic group in a polymer chain of a star polymer to be used according to the present invention include the following, provided that the present invention is not limited thereto.

[0058]

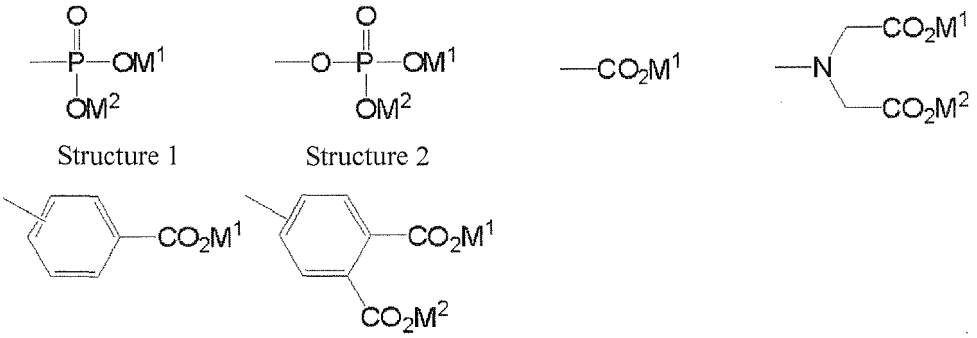




[0059] A star polymer to be used according to the present invention may contain a recurring unit having one kind of hydrophilic group or a recurring unit having 2 or more kinds of hydrophilic groups.
The content of a recurring unit having a hydrophilic group in a polymer chain of a star polymer to be used according to the present invention is preferably 30 to 98 mol-% based of the total recurring units contained in a star polymer, more preferably 40 to 90 mol-%, and further preferably 50 to 90 mol-%.

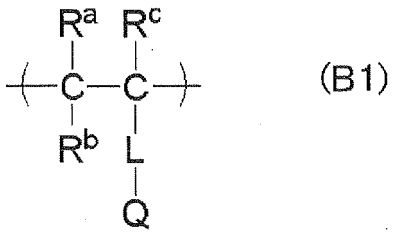
(Substrate adsorptive group)

[0060] Preferably, a polymer chain of a star polymer to be used according to the present invention contains at least one functional group, which can be adsorbed on the surface of a substrate by interacting with the surface of a substrate (herein referred to as a "substrate adsorptive group"), in order to enhance adherence to a substrate. More preferably, a polymer chain of a star polymer to be used according to the present invention contains a recurring unit having at least one substrate adsorptive group as a copolymer component. Examples of a functional group, which can be adsorbed by interacting with the surface of a substrate, include a group, which can interact with a metal, a metallic oxide, a hydroxy group, *etc.* existing on a substrate subjected to an anodizing treatment or a hydrophilizing treatment, through an ionic bond, a hydrogen bond, a polar interaction, *etc.* Examples of the substrate adsorptive group include a phosphonic acid group or a salt thereof, a phosphoric ester group or a salt thereof, and a carboxylic acid group or a salt thereof. A polymer chain of a star polymer to be used according to the present invention may contain one kind, or two or more kinds of such substrate adsorptive groups.
While, in a star polymer to be used according to the present invention, a hydrophilic group and a substrate adsorptive group are different group from each other. Therefore, if a star polymer has at least one hydrophilic group and at least one substrate adsorptive group, it has namely at least two kinds of functional groups.
Specific examples of a substrate adsorptive group include the following.
[0061]



[0062] In the formula, M^1 and M^2 independently represent a hydrogen atom, a metal atom belonging to an alkali metal or an alkaline earth metal, or an ammonium group. From a viewpoint of resistance to dirt, at least one of a substrate adsorptive group should be preferably selected from a phosphonic acid group or a salt thereof (structure 1), a phosphoric ester group or a salt thereof (structure 2), and a carboxylic acid group or a salt thereof; and among others a phosphoric ester group or a salt thereof, and a phosphonic acid group or a salt thereof are preferable. Specific examples of a recurring unit having at least one substrate adsorptive group in a polymer chain of a star polymer to be used according to the present invention are preferably represented by the following general formula (B1).

[0063]

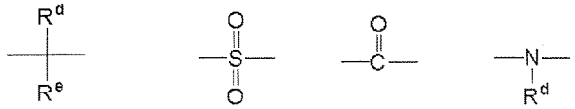


(B1)

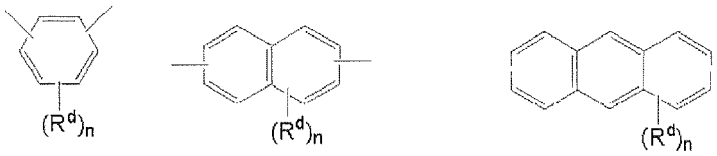
wherein R^a to R^c independently represent a hydrogen atom, a C1 to C6 alkyl group, or a halogen atom. Q represents a substrate adsorptive group, whose preferable embodiments are same as above.

L is a single bond, or a divalent linking group. The divalent linking group is constituted of 1 to 60 carbon atoms, 0 to 10 nitrogen atoms, 0 to 50 oxygen atoms, 1 to 100 hydrogen atoms, and 0 to 20 sulfur atoms; and more specifically examples thereof include those constituted of a combination of the following structure units.

[0064]



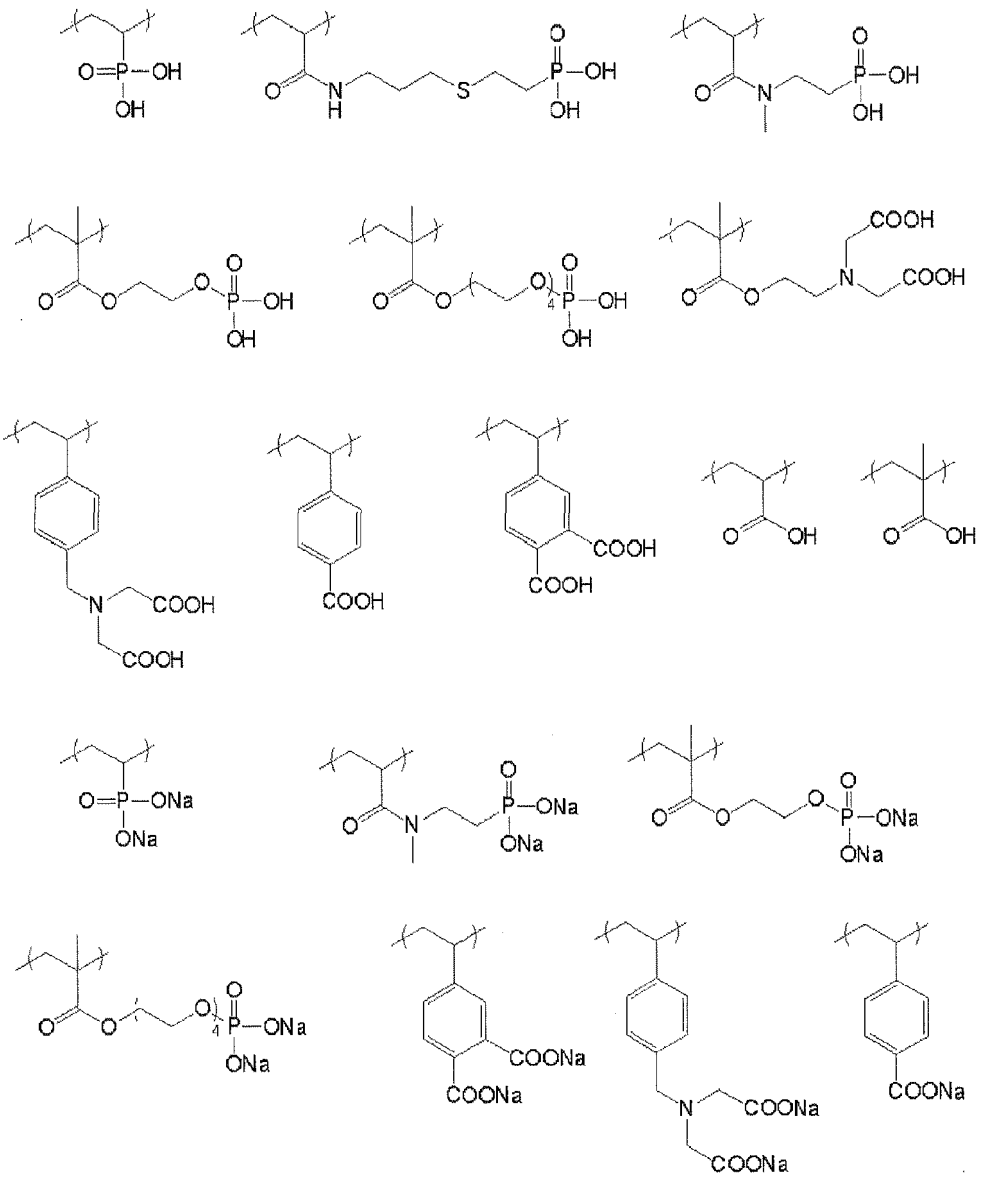
—O—



wherein R^d and R^e represent a hydrogen atom, a C1 to C20 alkyl group, a C6 to C20 aryl group, or a halogen atom. The n represents an integer of 1 to 4.

[0065] Specific examples of a recurring unit having at least one substrate adsorptive group to be used according to the present invention are shown below, provided that the present invention is not limited thereto.

[0066]



[0067] A star polymer according to the present invention may contain one kind, or two or more kinds of substrate adsorptive groups in it.
The content of a recurring unit having a substrate adsorptive group in a polymer chain of a star polymer usable according to the present invention is preferably 2 to 80 mol-% based on the total recurring units included in the star polymer, more preferably 2 to 70 mol-%, further preferably 5 to 50 mol-%, and especially preferably 10 to 40 mol-%.

(Other recurring unit)

[0068] A polymer chain of a star polymer to be used according to the present invention may be a copolymer containing a recurring unit other than the above (hereinafter occasionally referred to simply as "(an)other recurring unit"). Examples of another recurring unit include such recurring units as originated from a heretofore known variety of monomers.

[0069] A polymer chain of a star polymer to be used according to the present invention may contain, in addition to the above described recurring unit having a hydrophilic group and recurring unit having a substrate adsorptive group, for example, a polymerized unit of an alkyl or aralkyl (meth)acrylate, or a polymerized unit of a styrene derivative.
An alkyl group of an alkyl (meth)acrylate is preferably a C1 to C5 alkyl group, or an C2 to C 8 alkyl group having the aforedescribed substituent, and more preferably a methyl group. Examples of an aralkyl (meth)acrylate include benzyl (meth) acrylate.
Examples of a styrene derivative include styrene, and 4-*tert*-butylstyrene.

[0070] The content of another recurring unit in a polymer chain of a star polymer usable according to the present

invention is preferably 40 mol-% or less based on the total recurring units included in the star polymer, more preferably 30 mol-% or less, and further preferably 20 mol-% or less.

[0071] For a combination of a recurring unit having a substrate adsorptive group and a recurring unit having a hydrophilic group in a star polymer to be used according to the present invention, preferably a substrate adsorptive group is a phosphonic acid group or a salt thereof, a phosphoric ester group or a salt thereof, or a carboxylic acid group or a salt thereof, and a hydrophilic group is a sulfonic acid group or a salt thereof, an amide group, a polyalkylene oxide group, a hydroxy group, or a betaine structure; more preferably a substrate adsorptive group is a phosphonic acid group or a salt thereof, or a phosphoric ester group or a salt thereof, and a hydrophilic group is a sulfonic acid group or a salt thereof, a polyalkylene oxide group, a hydroxy group, or a betaine structure; and especially preferably a substrate adsorptive group is a phosphonic acid group or a salt thereof, or a phosphoric ester group or a salt thereof, and a hydrophilic group is a sulfonic acid group or a salt thereof, a polyalkylene oxide group, or a hydroxy group.

[0072] The mass average molar mass (Mw) of the star polymer is preferably 5,000 or higher, more preferably 10,000 or higher, but preferably 1,000,000 or lower, more preferably 500,000 or lower.

The number average molar mass (Mn) of the star polymer is preferably 1,000 or higher, more preferably 2,000 or higher, but preferably 500,000 or lower, more preferably 300,000 or lower.

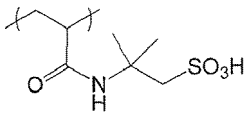
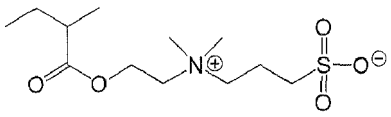
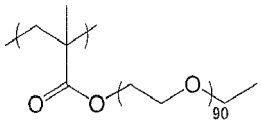
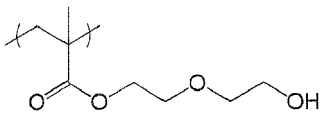
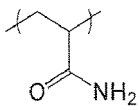
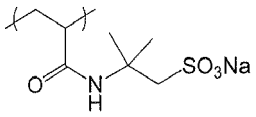
The polydispersity (Mw/Mn) of the star polymer is preferably 1.1 to 10.

[0073] Specific examples of a star polymer to be used according to the present invention are listed in Tables 7 to 12, provided that the present invention is not limited thereto.

Star polymers shown in Table 7 to 12 include polymers P_A -1, 2 and so forth, whose polymer chain has a structure constituted of a recurring unit (A) having a hydrophilic group, as well as polymers P_{AB} -1, 2 and so forth, whose polymer chain has a structure constituted of a recurring unit (A) having a hydrophilic group and a recurring unit (B) having a substrate adsorptive group.

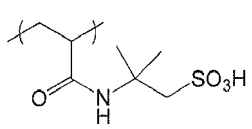
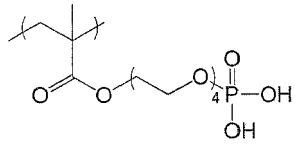
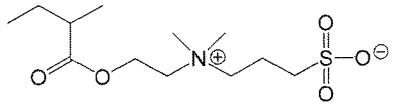
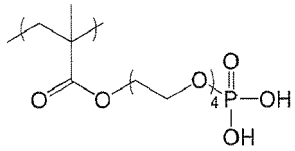
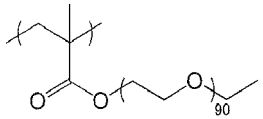
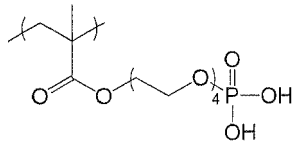
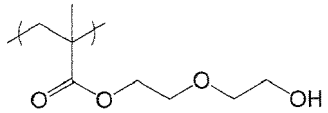
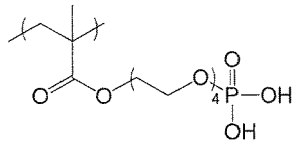
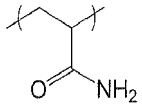
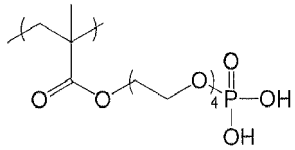
[0074]

[Table 7]

Polymer number	Skeleton		Hydrophilic group	Mw
	Number	Molar ratio		
P_A-1	SA-8	1		41,000
P_A-2	SA-8	1		45,000
P_A-3	SA-8	1		49,000
P_A-4	SA-8	1		42,000
P_A-5	SA-8	1		40,000
P_A-6	SA-8	1		40,000

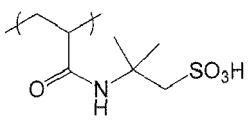
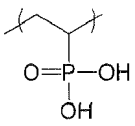
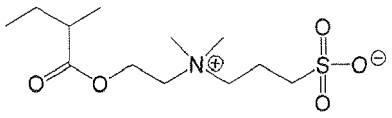
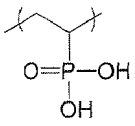
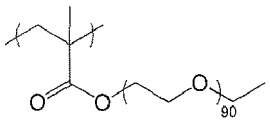
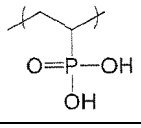
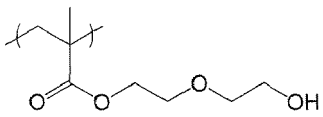
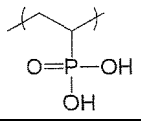
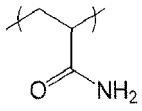
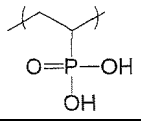
[0075]

[Table 8]

Polymer number	Skeleton		Polymer chain			
	Number	mol-%*1	Hydrophilic group recurring unit (A)	Substrate adsorptive group recurring unit (B)	(A)/(B) molar ratio	Mw
P_{AB}-1	SA-8	1			80/20	41,000
P_{AB}-2	SA-8	1			80/20	42,000
PAY-3	SA-8	1			80/20	48,000
P_{AB}-4	SA-8	1			80/20	4,000
P_{AB}-5	SA-8	1			80/20	38,000
*1 : equivalent of SH taking monomer as 100						

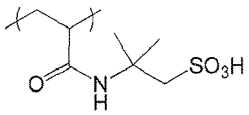
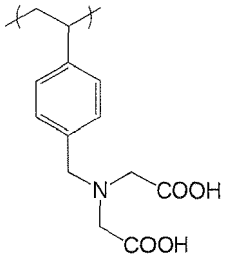
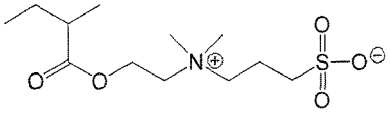
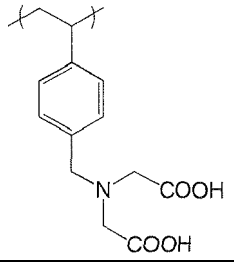
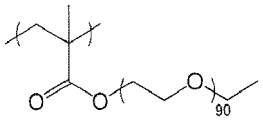
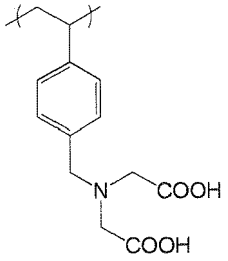
[0076]

[Table 9]

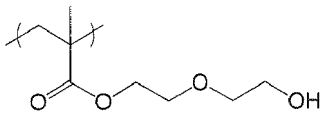
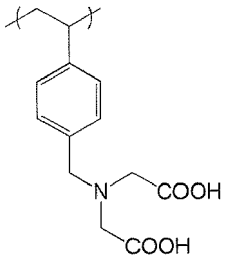
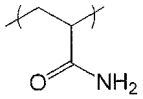
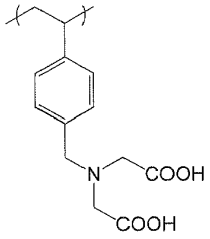
P_{AB}-6	SA-8	1			80/20	39,000
P_{AB}-7	SA-8	1			80/20	42,000
P_{AB}-8	SA-8	1			80/20	46,000
P_{AB}-9	SA-8	1			80/20	39,000
P_{AB}-10	SA-8	1			80/20	37,000

[0077]

[Table 10]

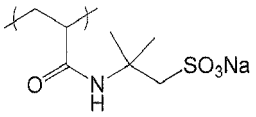
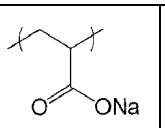
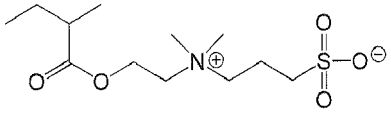
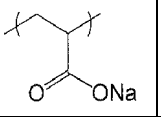
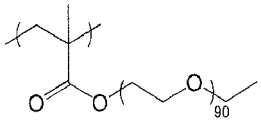
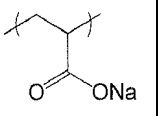
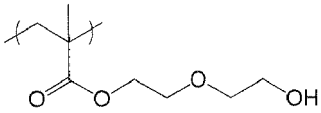
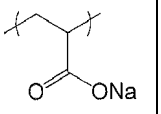
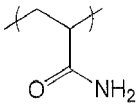
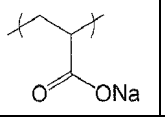
P_{AB}-11	SA-8	1			80/20	41,000
P_{AB}-12	SA-8	1			80/20	43,000
P_{AB}-13	SA-8	1			80/20	50,000

(continued)

P_{AB}-14	SA-8	1			80/20	41,000
P_{AB}-15	SA-8	1			80/20	40,000

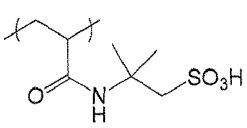
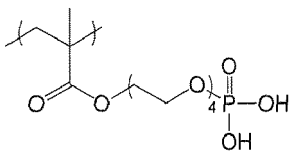
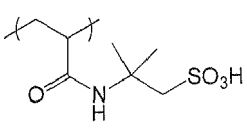
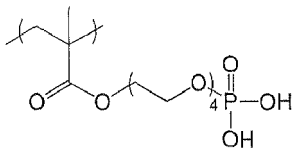
[0078]

[Table 11]

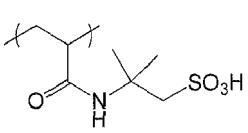
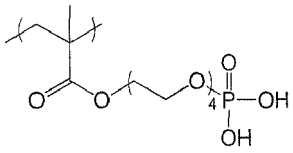
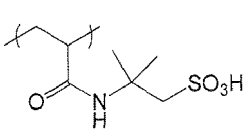
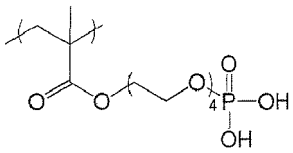
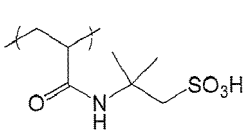
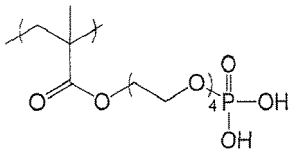
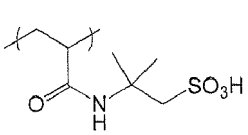
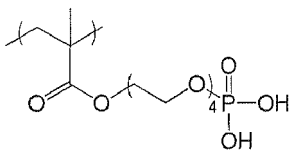
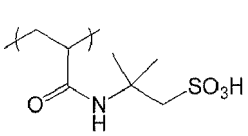
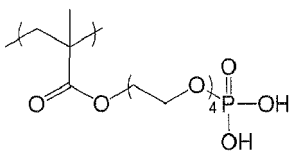
P_{AB}-16	SA-8	1			80/20	39,000
P_{AB}-17	SA-8	1			80/20	41,000
P_{AB}-18	SA-8	1			80/20	44,000
P_{AB}-19	SA-8	1			80/20	39,000
P_{AB}-20	SA-8	1			80/20	36,000

[0079]

[Table 12]

P_{AB}-21	SA-1	1			80/20	105,000
P_{AB}-22	SA-6	1			80/20	56,000

(continued)

P_{AB}-23	SB-205	1			80/20	58,000
P_{AB}-24	SC-100	1			80/20	55,000
P_{AB}-25	SE-107	1			80/20	52,000
P_{AB}-26	SE-109	1			80/20	54,000
P_{AB}-27	SF-58	1			80/20	50,000

[0080] A fountain solution composition for lithographic printing according to the present invention may contain a single kind of star polymer or 2 or more kinds.
The appropriate content of a star polymer in a fountain solution composition for lithographic printing according to the present invention is in general 0.005 to 10 mass-% with respect to a fountain solution before using, and within the range a dirt prevention effect on a non-image area and a mesh image area can be obtained sufficiently. The content is more preferably 0.01 to 5 mass-% and further preferably 0.1 to 3 mass-%.
A fountain solution composition is preferably used by diluting appropriately a concentrated solution generally before using, and a dilution rate of approx. 10 to 200-fold is appropriate, and especially approx. 30 to 100 is preferable. If the concentration rate is too high, such troubles as deposition, or liquid separation in a concentrated solution are apt to happen. Hereinafter a fountain solution composition ready for use is called simply as a "fountain solution".

[II] Other component

[0081] Preferably as a solubilizer in preparing a concentrated solution, compounds according to the following general formula (I) are used, by which the advantageous effects of the present invention can be synergistically enhanced.

[0082] Compounds according to the formula (I):

$$R^1\text{-}O\text{-}(CH_2\,CHR^2\,O)_m\text{-}H \qquad (I)$$

wherein R^1 represents a C1 to C4 alkyl group or an OH group, R^2 represents a hydrogen atom or a methyl group, and m represents an integer of 1 to 5.
Specifically, in a compound according to the formula (I), R^1 in the formula represents an OH group or a C1 to C4 alkyl group with a straight chain or a branched chain; and specific examples thereof include an OH group, a methyl group, an ethyl group, a propyl group, an isopropyl group, an *n*-butyl group, an isobutyl group, and a t-butyl group; and among others an OH group, an *n*-butyl group and a t-butyl group are especially preferable. Further, m represents an integer of 1 to 5, and an integer of 1 to 3 is preferable, and especially preferable 1.

[0083] Specific examples, when R^1 in the general formula (I) is an alkyl group, include ethylene glycol mono-*t*-butyl ether, ethylene glycol mono-*n*-butyl ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, propylene glycol monoethyl ether, dipropylene glycol monoethyl ether, tripropylene

glycol monoethyl ether, tetrapropylene glycol monoethyl ether, propylene glycol monopropyl ether, dipropylene glycol monopropyl ether, tripropylene glycol monopropyl ether, propylene glycol monoisopropyl ether, dipropylene glycol monoisopropyl ether, tripropylene glycol monoisopropyl ether, propylene glycol monon-butyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monobutyl ether, propylene glycol monoisobutyl ether, dipropylene glycol monoisobutyl ether, tripropylene glycol monoisobutyl ether, propylene glycol mono-*tert*-butyl ether, dipropylene glycol mono-*tert*-butyl ether and tripropylene glycol mono-*tert*-butyl ether. Among others, *n*-butyl or t-butyl ether of propylene glycol or ethylene glycol can be used favorably.

[0084] Specific examples, when R^1 in the general formula (I) is an OH group, include propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol and pentapropylene glycol. Among others, in order to improve solubility of a diol compound, propylene glycol, dipropylene glycol, and tripropylene glycol are preferable, and propylene glycol is most preferable.

[0085] As a compound expressed by the general formula (I) are used preferably a plurality of compounds listed above in a combination, and especially if a compound whose R^1 is an alkyl group and a compound whose R^1 is an OH group are used in a combination, the activity for suppressing blanket piling can be high, and further roller stripping, *etc.* can be prevented.

[0086] A fountain solution composition according to the present invention can use as a fountain solvent 3-methoxy-3-methylbutanol, 3-methoxybutanol, ethylene glycol, diethylene glycol, triethylene glycol, butylene glycol, hexylene glycol, glycerol, diglycerol, polyglycerol, trimethylol propane, *etc.*

The solvent is used in a range of 0.1 to 3 mass-% with respect to the fountain solution, and preferably in a range of 0.3 to 2 mass-%.

[0087] A fountain solution composition according to the present invention may contain also water soluble polymeric compounds used conventionally in a fountain solution composition in addition to a star polymer described above.

Examples of a water soluble polymeric compound to be used in a fountain solution composition according to the present invention include a natural product and a modification thereof, such as gum arabic, a starch derivative *(e.g.,* dextrin, enzyme-degraded dextrin, hydroxypropyl enzyme-degraded dextrin, carboxymethyl starch, starch phosphate , and octenyl succinate starch), an alginic acid salt, a cellulose derivative *(e.g.,* carboxymethylcellulose, carboxyethyl cellulose, methylcellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, and hydroxyethyl cellulose); and a synthetic product, such as polyethylene glycol and a copolymer thereof, polyvinyl alcohol and a derivative thereof, polyvinylpyrrolidone, polyacrylamide and a copolymer thereof, polyacrylic acid and a copolymer thereof, a vinyl methyl ether/maleic anhydride copolymer, a vinyl acetate/ maleic anhydride copolymer, and polystyrene sulfonic acid and a copolymer thereof. Among the water soluble polymeric compounds carboxymethyl cellulose, polyvinylpyrrolidone, hydroxypropyl cellulose, and hydroxypropylmethyl cellulose can be used especially favorably.

The molecular weight of the water soluble polymeric compound is preferably 300 to 500,000, more preferably 300 to 100,000, and especially preferably 500 to 30,000.

An appropriate content of a water soluble polymeric compound is 0.0001 to 0.1 mass-% with respect to the fountain solution, and more preferably 0.0005 to 0.05 mass-%.

[0088] A fountain solution composition according to the present invention is preferably further adjusted to a favorable pH value with a pH adjustor. It is preferably used in an acidic range with a pH value of 3 to 7, but it can also be used in an alkali range of pH 7 to 11. As the pH adjustor a water soluble organic or inorganic acid and a salt thereof can be used. Examples of a preferable organic acid include acetic acid, citric acid, oxalic acid, malic acid, tartaric acid, succinic acid, lactic acid, ascorbic acid, gluconic acid, hydroxyacetic acid, malonic acid, levulinic acid, sulfanilic acid, p-toluenesulfonic acid, phytic acid, and an organic phosphonic acid; examples of an inorganic acid include phosphoric acid, nitric acid, sulfuric acid, and polyphosphoric acid; and an alkali metal salt, an alkaline earth metal salt, an ammonium salt, and an organic amine salt thereof can be also favorably used. They may be used as a mixture of two or more. The content of such a pH adjustor in a fountain solution is generally in a range of 0.001 to 0.3 mass-%.

[0089] A fountain solution composition according to the present invention contains preferably further as an aid for improving wettability a pyrrolidone derivative, acetylene glycols or acetylene alcohols. Examples of a pyrrolidone derivative include ethylpyrrolidone, butylpyrrolidone, pentapyrrolidone, hexapyrrolidone, octylpyrrolidone, and laurylpyrrolidone; and examples of acetylene glycols and acetylene alcohols include 3,5-dimethyl-1-hexyn-3-ol., 2,5-dimethyl-3-hexyne-2,5-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, 3,6-dimethyl-4-octyne-3,6-diol, 2-butyne-1,4-diol, and 3-methyl-l-butyn-3-ol, as well as an addition product of the same with ethylene oxide and/or propylene oxide. Among the above compounds, especially compounds of octylpyrrolidone, 3,6-dimethyl-4-octyne-3,6-diol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol, and 2,4,7,9-tetramethyl-5-decyne-4,7-diol, to which 4 to 10 ethylene oxide units are added, are preferable. They should be preferably used in an amount of 0.0001 to 1.0 mass-% with respect to a fountain solution, and more preferably 0.001 to 0.1 mass-%.

[0090] A fountain solution composition according to the present invention contains preferably further 2-ethyl-1,3-hexanediol, an adduct of 2-ethyl-1,3-hexanediol with ethylene oxide and/or propylene oxide, an adduct of trimethylol propane with propylene oxide, an adduct of glycerol with propylene oxide, an adduct of sorbitol with propylene oxide, tetrahydro-

furfuryl alcohol, *etc.* for adjustment of dynamic surface tension, solubilization, control of mixing rate of ink (emulsification rate) in a proper range, *etc.;* and especially preferably contains 2-ethyl-1,3-hexanediol, as well as tetrahydrofurfuryl alcohol as a solubilizer. A compound listed above should be used at an appropriate content of 0.01 to 7 mass-% with respect to a fountain solution, and more preferably at 0.05 to 5 mass-%.

[0091] As another component, a fountain solution composition according to the present invention may additionally contain, for example, a compound derived from ethylenediamine or diethylenetriamine by adding ethylene oxide and propylene oxide, and such a compound does not inflict damages to an image area, even if a residual aqueous drop is left standing on a plate and concentrated by water evaporation while a printing press is stopped. The addition mole number ratio of ethylene oxide to propylene oxide thereof is preferably in a range of 5/95 to 50/50, and more preferably in a range of 20/80 to 35/65. Each copolymer chain may have a block structure or a random structure. The weight-average molecular weight of the addition compound used according to the present invention is preferably 500 to 5000, more preferably 800 to 1500, and optimally the weight-average molecular weight is about 1000. The molecular weight and the ratio of ethylene oxide to propylene oxide can be determined by measurements of hydroxyl value and amine value, NMR analysis, etc.

By containing the compound at 0.01 to 1 mass-%, preferably 0.05 to 0.5 mass-%, in a fountain solution composition in use, good printing quality can be attained, even if isopropyl alcohol is replaced.

[0092] A fountain solution composition according to the present invention can use a surfactant as an aid for wettability improvement. With respect to a surfactant, examples of an anionic surfactant include a fatty acid salt, an abietate, a hydroxyalkanesulfonate, an alkanesulfonate, a dialkylsulfosuccinate, an alkylbenzenesulfonate, an alkylnaphthalenesulfonate, an alkylphenoxypolyoxyethylene propylsulfonate, a polyoxyethylene alkylsulfenyl ether salt, an N-methyl-N-oleyltaurine sodium salt, an N-alkylsulfosuccinate monoamide disodium salt, a petroleum sulfonate, sulfated castor oil, sulfated tallow, a sulfate salt of a fatty acid alkyl ester, an alkylsulfate salt, a polyoxyethylene alkyl ether sulfate salt, a fatty acid monoglyceride sulfate salt, a polyoxyethylene alkylphenyl ether sulfate salt, a polyoxyethylene styryl phenyl ether sulfate salt, an alkylphosphate salt, a polyoxyethylene alkyl ether phosphate salt, a polyoxyethylene alkylphenyl ether phosphate salt, a partially saponified styrene-maleic anhydride copolymer, a partially saponified olefin-maleic anhydride copolymer, and a condensation product between naphthalenesulfonic acid salt and formalin. Among them, a dialkylsulfosuccinate, an alkylsulfate salt, and an alkylnaphthalenesulfonate are especially preferable.

[0093] Examples of a nonionic surfactant include a polyoxyethylene alkyl ether, a polyoxyethylene alkylphenyl ether, a polyoxyethylene polystyryl phenyl ether, a polyoxyethylene polyoxypropylene alkyl ether, a partial ester of glycerol and a fatty acid, a partial ester of sorbitan and a fatty acid, a partial ester of pentaerythritol and a fatty acid, a propylene glycol mono-fatty acid ester, a partial ester of sucrose and a fatty acid, a partial ester of polyoxyethylene sorbitan and a fatty acid, a partial ester of polyoxyethylene sorbitol and a fatty acid, a polyethylene glycol fatty acid ester, a partial ester of polyglycerol and a fatty acid, a polyoxyethylene castor oil, a partial ester of polyoxyethylene glycerol and a fatty acid, a fatty acid diethanolamide, an *N,N* bis-2-hydroxyalkylamine, a polyoxyethylene alkylamine, a triethanolamine fatty acid ester, and a trialkylamine oxide.

Among them, a polyoxyethylene alkyl ether, a polyoxyethylene alkylphenyl ether, a polyoxyethylene-polyoxypropylene block copolymer, and polyoxyethylene castor oil ether can be favorably used.

Further, a fluorinated surfactant, and a silicone surfactant can be used.

If a surfactant is used, considering foaming, the content of 1.0 mass-% or less, preferably 0.001 to 0.5 mass-%, with respect to a fountain solution is appropriate.

[0094] A fountain solution composition according to the present invention may contain also a sugar. A sugar to be used includes a sugar alcohol produced by hydrogenation.

Specific examples of a preferable sugar include D-erythrose, D-threose, D-arabinose, D-ribose, D-xylose, D-erythro-pentulose, D-allulose, D-galactose, D-glucose, D-mannose, D-talose, β-D-fructose, α-L-sorbose, 6-deoxy-D-glucose, D-glycero-D-galactose, α-D-allo-heptulose, β-D-altro-3-heptulose, saccharose, lactose, D-maltose, isomaltose, inulobiose, hyaluronic acid, maltotriose, D,L-arabitol, ribitol, xylitol, D,L-sorbitol, D,L-mannitol, D,L-iditol, D,L-talitol, dulcitol, allodulcitol, and maltitol. The sugars may be used singly or in a combination of 2 or more.

An appropriate content of a sugar with respect to a fountain solution is 0.01 to 1 mass-%, and preferably 0.1 to 0.8 mass-%.

[0095] With respect to a fountain solution composition according to the present invention, a calcium ion, etc. contained in tap water or well water for diluting a concentrated solution before using may affect printing negatively and make a print susceptible to dirt. In such a case, addition of a chelating agent can overcome the drawback. Examples of a preferable chelating agent include a potassium salt or a sodium salt of the acid listed below. Examples of the acid include an organic phosphonic acid, such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, triethylenetetraminehexaacetic acid, hydroxyethylethylenediaminetriacetic acid, nitrilotriacetic acid, 1-hydroxyethane-1,1-diphosphonic acid, and aminotri(methylenephosphonic acid), as well as a phosphonoalkanetricarboxylic acid. In place of a sodium salt or a potassium salt of the chelating agent, a salt of an organic amine can be also used effectually.

A chelating agent, which can be stably present in a fountain solution composition in use without disturbing printing, is selected among them. An appropriate content of a chelating compound in a fountain solution composition in use is 0.001

to 0.5 mass-% and preferably 0.002 to 0.25 mass-%.

[0096] A fountain solution composition according to the present invention may contain as an odor masking reagent an ester, which has been heretofore known for use as a fragrance. Preferable examples thereof include *n*-pentyl acetate, isopentyl acetate, *n*-butyl butyrate, *n*-pentyl butyrate and isopentyl butyrate; and especially *n*-butyl butyrate, *n*-pentyl butyrate and isopentyl butyrate are favorable.

[0097] A fountain solution composition according to the present invention may contain an antiseptic agent; and examples of an antiseptic agent include phenol or a derivative thereof, formalin, an imidazole derivative, sodium dehydroacetate, a 4-isothiazolin-3-one derivative, a benztriazole derivative, a derivative of amidine or guanidine, a quaternary ammonium salt, pyridine, a derivative of quinoline or guanidine, a derivative of diazine or triazole, a derivative of oxazole or oxazine, bromonitropropanol of a bromonitroalcohol, 2,2-dibromo-2-nitroethanol, and 3-bromo-3-nitropentane-2,4-diol. A preferable addition amount is an amount, which can exert stably activity against bacteria, fungi, yeast, *etc.,* and is preferably in a range of 0.001 to 1.0 mass-% with respect to a fountain solution. Antiseptic agents should preferably be used in a combination of 2 or more thereof, which have respectively activity against certain fungi, bacteria or yeast.

[0098] A fountain solution composition according to the present invention can favorably use a food dye as a colorant, and examples thereof include, as a yellow dye, C.I. No. 19140, 15985; as a red dye, C.I. No. 16185, 45430, 16255, 45380, 45100; as a purple dye, C.I. No. 42640; as a blue dye, C.I. No. 42090, 73015; and as a green dye, C.I. No. 42095. Examples of an anti-corrosive agent usable according to the present invention include benzotriazole, 5-methylbenzotriazole, thiosalicylic acid, benzoimidazole, and a derivative thereof.

As a defoaming agent usable according to the present invention, a silicone defoaming agent is preferable, for which both an emulsion type and a solution type can be used.

[0099] The balance component of a fountain solution composition according to the present invention is water. For merchandizing a fountain solution composition is in general concentrated and packaged. Accordingly, the aforedescribed components are dissolved in water, preferably in desalted water, namely pure water, to an aqueous solution to prepare a concentrated solution. When such a concentrated solution is used, it is diluted generally before using by tap water, well water, *etc.* 10 to 200-fold, preferably approx. 30 to 100-fold, to a ready-for-use fountain solution composition.

The present invention is also directed to a fountain solution composition for lithographic printing in a form of a concentrated solution. For preparation of a concentrated solution, an appropriate concentration rate is selected so that deposition or liquid separation in a concentrated solution can be prevented, and that a ready-for-use fountain solution composition containing the components at proper concentrations can be prepared by dilution at a proper dilution rate.

As an exemplar formation of a concentrated fountain solution composition for lithographic printing according to the present invention, there is a concentrated fountain solution containing the star polymer in a range of 0.5 to 10 mass-%. A further specific example include a formation containing the star polymer in a range of 0.5 to 10 mass-%, a compound according to the general formula (I) from 1 to 80 parts by mass with respect to 1 part by mass of the star polymer, a water soluble polymeric compound other than the star polymer from 0.5 to 10 parts by mass, at least one selected out of an organic acid, an inorganic acid, and a salt thereof from 0.5 to 10 parts by mass, an antiseptic agent from 0.1 to 2.0 parts by mass, optionally another component, and water as the balance.

[0100] Although a fountain solution composition according to the present invention can be applied to various lithographic plates, it can be favorably applied especially to a lithographic plate prepared by exposing and developing an image on a photosensitive lithographic plate having a photosensitive layer on a substrate aluminum plate.

Examples of a preferable PS plate include that with a photosensitive layer composed of a mixture of a diazo resin (a salt of a condensation product between *p*-diazodiphenylamine and paraformaldehyde) and shellac provided on an aluminum plate as described in GB Patent No. 1,350,521; that with a photosensitive layer composed of a mixture of a diazo resin and a polymer having a hydroxyethyl methacrylate unit or a hydroxyethyl acrylate unit as a major recurring unit provided on an aluminum plate as described respectively in GB Patent No. 1,460,978 and GB Patent No. 1,505,739; a negative PS plate with a photosensitive polymer system containing a dimethylmaleimide group provided on an aluminum plate as described in Japanese Published Unexamined Application No. 2-236552, and Japanese Published Unexamined Application No. 4-274429; and a positive PS plate with a photosensitive layer composed of a mixture of an *o*-quinonediazide photosensitive material and a novolac-type phenolic resin provided on an aluminum plate as described in Japanese Published Unexamined Application No. 50-125806.

Further, it can be applied also to a positive PS plate subjected to a burning treatment.

[0101] To the composition forming a photosensitive layer, an alkali-soluble resin other than the alkali-soluble novolac resin can be added according to need.

Examples thereof include a styrene-acrylic acid copolymer, a methyl methacrylate-methacrylic acid copolymer, an alkali-soluble polyurethane resin, an alkali-soluble vinyl resin according to Japanese Published Examined Application 52-28401, and an alkali-soluble polybutyral resin.

Further, a PS plate with a photosensitive layer of a light-polymerizing photopolymer composition provided on an aluminum plate as described respectively in US Patent No. 4,072,528 and US Patent No. 4,072,527, and a PS plate with a photosensitive layer composed of a mixture of an azide and a water-soluble polymer provided on an aluminum plate as

described respectively in GB Patent No. 1,235,281 and GB Patent 1,495,861 are also preferable.
Further, it is favorably applicable to a CTP plate, which is directly exposed by a visible or infrared laser. Specific examples thereof include a photopolymer type digital plate (e.g. LP-NX by Fujifilm Corporation), a thermal positive type digital plate *(e.g.* LH-PI by Fujifilm Corporation), a type of plate, which is developed on a printing press by a fountain solution and an ink *(e.g.* ET-S by Fujifilm Corporation), and a thermal negative-type digital plate (e.g. LH-NI by Fujifilm Corporation).

[Example]

[0102] The present invention will be described more specifically below by way of Examples and Comparative Examples, provided that the examples should not be considered to limit the scope of the invention in any way. While with respect to a macromolecular compound, unless otherwise specified, the molecular weight is in mass average molar mass (Mw), and the content of a recurring unit is in molar percentage.

[Examples 1 to 6 and Comparative Examples 1 to 2]

[Preparation of thermal negative-type digital plate]

[Preparation of substrate]

[0103] A 0.30 mm-thick aluminum plate (aluminum alloy containing Si: 0.09 mass-%, Fe: 0.30 mass-%, Cu: 0.013 mass-%, Mn: 0.001 mass-%, Mg: 0.001 mass-%, Zn: 0.001 mass-%, Ti: 0.027 mass-%, Al and incidental impurities: the balance) was subjected continuously to the following surface treatments (a) to (k)
While a liquid was remove by nip rollers after respective treatments and water washing.

(a) Mechanical surface roughening treatment

[0104] While supplying a suspension liquid of a polishing material (pumice) with the specific gravity 1.12 in water as an abrasive slurry to a surface of an aluminum plate, a mechanical surface roughening treatment was carried out by a revolving roller-shaped nylon brush.
The average particle size of the polishing material was 30 μm, and the maximum particle size was 100 μm.
The material of the nylon brush was 6.10-nylon, the bristle length was 45 mm, and the bristle diameter was 0.3 mm. The nylon brush was constructed by boring holes in a 300 mmΦ-stainless steel cylinder and planting bristles dense thereto. Three revolving brushes were used. The brush roller was so pressed to an aluminum plate that the load of a driving motor for revolving the brush increased by 7 kW compared to the load before pressing. The rotational direction of the brush was identical with the travelling direction of an aluminum plate. The revolving rate of the brush was 200 rpm.

(b) Alkali etching treatment

[0105] The thus prepared aluminum plate was subjected to an etching treatment by spraying an aqueous solution of caustic soda at a concentration of 2.6 mass-%, and aluminum ion at a concentration of 6.5 mass-% at a temperature of 70°C to dissolve the aluminum plate by 10 g/m^2 . Thereafter it was washed by water spraying.

(c) Desmutting treatment

[0106] A desmutting treatment was conducted by spraying an aqueous solution of 1 mass-% concentration nitric acid (containing 0.5 mass-% of aluminum ion) at a temperature of 30°C, followed by washing by water spraying. As the aqueous solution of nitric acid used for the desmutting treatment was utilized a waste fluid from a process step, in which an electrochemical surface roughening treatment was carried out using alternating current in an aqueous solution of nitric acid.

(d) Electrochemical surface roughening treatment

[0107] An electrochemical surface roughening treatment was conducted continuously using 60 Hz alternating voltage. The then electrolytic liquid was a 10.5 g/L nitric acid aqueous solution (containing 5 g/L of aluminum ion and 0.007 mass-% of ammonium ion) at the liquid temperature of 50°C. The electrochemical surface roughening treatment was conducted with a carbon electrode as a counter electrode using an alternating current power source giving trapezoidal (rectangular) alternating current with the TP of 0.8 msec (time from current zero to the peak current) and the duty ratio of 1/1. For an auxiliary anode, ferrite was used.

The current density at the current peak value was 30 A/dm^2 , and the quantity of electricity as the total quantity of electricity when an aluminum plate was an anode was 220 C/dm^2. To an auxiliary anode 5% of the current flown from the power source was shunted. Washing by water spraying was followed.

(e) Alkali etching treatment

[0108] An etching treatment was conducted on an aluminum plate at 32°C by spraying an aqueous solution of caustic soda at a concentration of 26 mass-%, and aluminum ion at a concentration of 6.5 mass-% to dissolve the aluminum plate by 0.50 g/m^2 , so that a smut component composed mainly of aluminum hydroxide formed during the upstream electrochemical surface roughening treatment using alternating current was removed, and the edges of formed pits were smoothed by dissolving the edges. Washing by water spraying was followed.

(f) Desmutting treatment

[0109] A desmutting treatment was conducted at 30°C by spraying a 15 mass-% aqueous solution of nitric acid (containing 4.5 mass-% of aluminum ion), followed by washing by water spraying. As the nitric acid solution used for desmutting was utilized a waste fluid from a process step, in which an electrochemical surface roughening treatment was carried out using alternating current in an aqueous solution of nitric acid.

(g) Electrochemical surface roughening treatment

[0110] An electrochemical surface roughening treatment was conducted continuously using 60 Hz alternating voltage. The then electrolytic liquid was a 5.0 g/L aqueous hydrochloric acid solution (containing 5 g/L of aluminum ion) at the temperature of 35°C. The electrochemical surface roughening treatment was conducted with a carbon electrode as a counter electrode using an alternating current power source giving trapezoidal (rectangular) alternating current with the TP of 0.8 msec (time from current zero to the peak current) and the duty ratio of 1/1. For an auxiliary anode, ferrite was used. The current density at the current peak value was 25 A/dm^2, and the quantity of electricity as the total quantity of electricity when an aluminum plate was an anode was 50 C/dm^2. Washing by water spraying was followed.

(h) Alkali etching treatment

[0111] An etching treatment was conducted on an aluminum plate at 32°C by spraying an aqueous solution of caustic soda at a concentration of 26 mass-%, and aluminum ion at a concentration of 6.5 mass-% to dissolve the aluminum plate by 0.10 g/m^2 , so that a smut component composed mainly of aluminum hydroxide formed during the upstream electrochemical surface roughening treatment using alternating current was removed, and the edges of formed pits were smoothed by dissolving the edges.

(i) Desmutting treatment

[0112] A desmutting treatment was conducted at 60°C by spraying a 25 mass-% aqueous solution of sulfuric acid (containing 0.5 mass-% of aluminum ion), followed by washing by water spraying.

(j) Anodizing treatment

[0113] An anodizing treatment was conducted using an anodizing apparatus (the 1st and the 2nd electrolytic part lengths 6 m respectively, the 1st and the 2nd power supply part lengths 3 m respectively, and the 1st and the 2nd power supply electrode part lengths 2.4 m respectively). As electrolytic solutions supplied to the 1 st and the 2nd electrolytic parts, sulfuric acid was used. For both the electrolytic solutions the concentration of sulfuric acid was 50 g/L (containing 0.5 mass-% of aluminum ion), and the temperature was 20°C. Washing by water spraying was followed.

(k) Alkali metal silicate treatment

[0114] An alkali metal silicate treatment (silicate treatment) was conducted by immersing an aluminum substrate prepared by an anodizing treatment in a treatment bath wirh a 1 mass-% aqueous solution of disodium trisilicate at a temperature of 30°C for 10 sec. Thereafter washing was carried out by spraying well water to obtain a substrate with a surface hydrophilized by the silicate treatment.

[0115] An aluminum plate subjected to all the treatment steps of (a) to (k) was defined as substrate S-1, whose center line average roughness (arithmetic average roughness Ra according to JIS B0601) was measured using a needle with

the diameter of 2 μm to find 0.50 μm for the substrate S-1.
Next the following prime coat coating liquid (A) was applied on to the aluminum substrate S-1 subjected to the aforedescribed surface treatments, to a dry coating weight of 10 mg/m^2, and followed by drying.

<Prime coat coating liquid (A)>

[0116]

polyvinylphosphonic acid (Mw 20000)	0.017 part by mass
methanol	9.00 parts by mass
water	1.00 part by mass

[Formation of photosensitive layer]

[0117] The following coating liquid (A) for a photosensitive layer was prepared and coated by a wire bar coater on the prime coat prepared as above to form a photosensitive layer. Drying was carried out by a hot air dyer at 125°C for 34 sec. The coating weight after drying was 1.4 g/m^2.

< Coating liquid (A) for photosensitive layer>

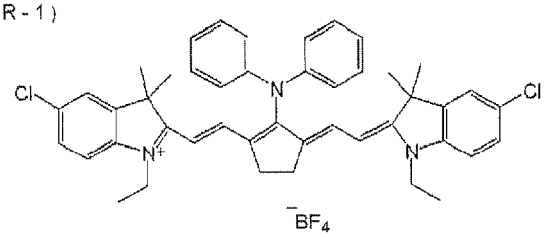
[0118]

infrared absorber (IR-1)	0.038 part by mass
polymerization initiator A (S-1)	0.061 part by mass
polymerization initiator B (I-1)	0.094 part by mass
mercapto compound (E-1)	0.015 part by mass
ethylenic unsaturated compound (M-1)	0.425 part by mass
(Trade name: A-BPE-4, by Shin-Nakamura Chemical Co., Ltd.) binder polymer A (B-1) (Mw: 110000)	0.311 part by mass
binder polymer B (B-2) (Mw: 100000)	0.250 part by mass
binder polymer C (B-3) (Mw: 120000)	0.062 part by mass
additive (T-1)	0.079 part by mass
polymerization inhibitor (Q-1)	0.0012 part by mass
ethyl violet (EV-1)	0.021 part by mass
fluorinated surfactant (Megafac F-780-F, by DIC; methyl isobutyl ketone (MIBK) 30 mass-% solution)	0.0081 part by mass
methyl ethyl ketone	5.886 parts by mass
methanol	2.733 parts by mass
1-methoxy-2-propanol	5.886 parts by mass

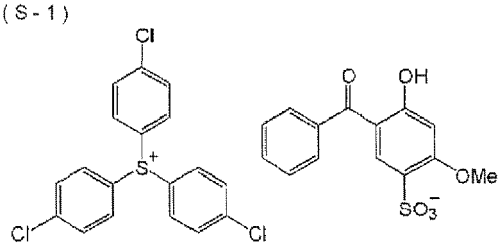
[0119] The structures of the infrared absorber (IR-1), the polymerization initiator A(S-1), the polymerization initiator B (I-1), the mercapto compound (E-1), the ethylenic unsaturated compound (M-1), the binder polymer A (B-1), the binder polymer B (B-2), the binder polymer C (B-3), the additive (T-1), the polymerization inhibitor (Q-1), and ethyl violet (EV-1) used for the coating liquid (A) for a photosensitive layer are shown below.
While, in the following, Me represents a methyl group, and the ratios of respective monomer units of the binder polymers A to C shown below are in molar ratio.

[0120]

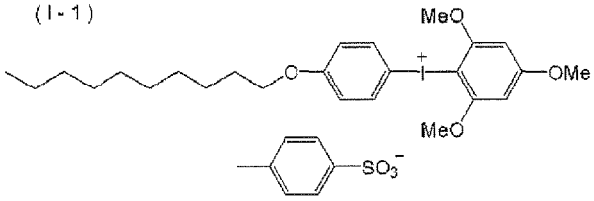
(IR-1)



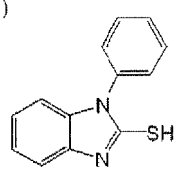
(S-1)



(I-1)

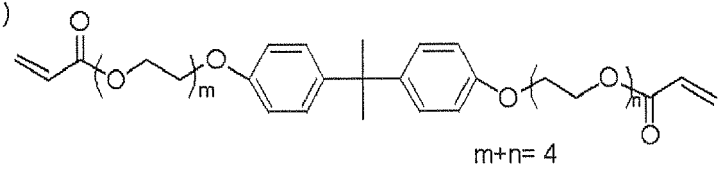


(E-1)

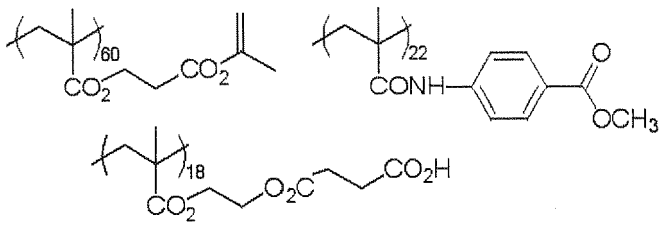


[0121]

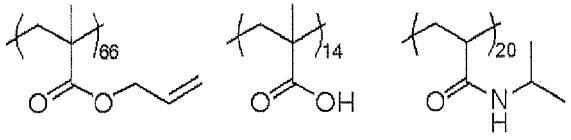
(M-1)



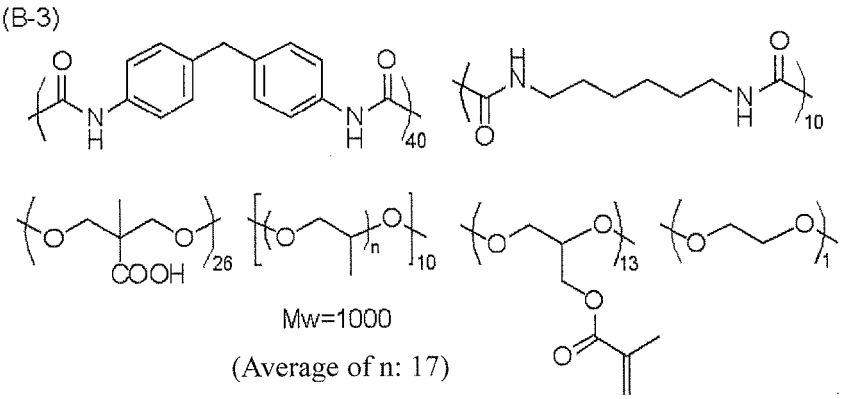
(B-1)



(B-2)

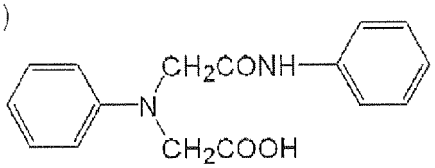


(B-3)

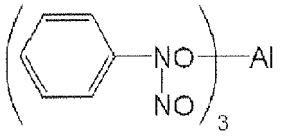


[0122]

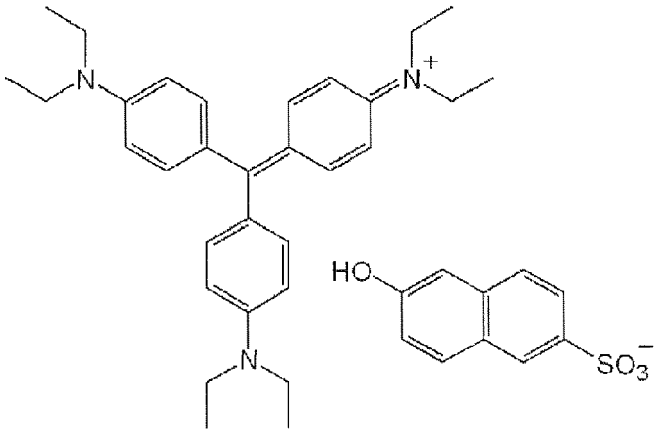
(T - 1)



(Q - 1)



(EV - 1)



[Formation of lower protective layer]

[0123] On to a formed photosensitive layer a mixed aqueous solution (a coating liquid for forming a lower protective layer) of synthetic mica (Somasif MEB-3L, 3.2 mass-% water dispersion, by Co-op Chemical Co., Ltd.), polyvinyl alcohol (Gohseran CKS-50, degree of saponification 99 mol-%, degree of polymerization 300, sulfonic acid modified polyvinyl alcohol, by The Nippon Synthetic Chemical Industry Co., Ltd.), a surfactant A (Emalex 710, by Nihon Emulsion Co., Ltd.), and a surfactant B (Adeka Pluronic P-84, by ADEKA Corporation) was coated by a wire bar coater and dried in a hot air dyer at 125°C for 30 sec.

In the coating liquid for a lower protective layer the content ratio of synthetic mica (solid portion)/polyvinyl alcohol/surfactant A/surfactant B was 7.5/89/2/1.5 (mass-%), and the coating amount (coating weight after drying) was 0.5 g/m^2 .

[Formation of upper protective layer]

[0124] On to the lower protective layer a mixed aqueous solution (a coating liquid for forming a upper protective layer) of an organic filler (Art-Pearl J-7P, by Negami Chemical Industrial Co., Ltd.), synthetic mica (Somasif MEB-3L, 3.2 mass-% water dispersion, by Co-op Chemical Co., Ltd.), polyvinyl alcohol (L-3266, degree of saponification 87 mol-%, degree of polymerization 300, sulfonic acid modified polyvinyl alcohol, by The Nippon Synthetic Chemical Industry Co., Ltd.), a thickening agent (Cellogen FS-B, by Dai-Ichi Kogyo Seiyaku Co., Ltd.), and a surfactant (Emalex 710, by Nihon Emulsion Co., Ltd.) was coated by a wire bar coater and dried in a hot air dyer at 125°C for 30 sec.
In the coating liquid for a upper protective layer the content ratio of organic fille/synthetic mica (solid portion)/polyvinyl alcohol/thickening agent/surfactant was 3.2/2.0/80.5/11.5/2.8 (mass-%) and the coating amount (coating weight after drying) was 1.76 g/m^2.

[Formation of back coat]

[0125] On to the surface of the aluminum substrate S-1 opposite to the side, on which a photosensitive layer and protective layers were provided, a back coat similar to example 1 of Japanese Published Unexamined Application No. 6-35174 was provided to obtain a negative lithographic original plate (1).

[Plate making process]

[0126] The obtained lithographic original plate was treated following the sequence of the steps of exposure, developing treatment , and plate surface treatment.
Image-wise exposure was carried out by a light source (setter) based on an infrared semiconductor laser (Trendsetter 3244VX: equipped with water-cooling 40 W infrared semiconductor laser, by Creo Inc. (Kodak)) under the conditions of the output power 9 W, the external drum rotation speed 210 rpm, and the resolution 2,400 dpi. As an exposed image an image with an array of reverse thin lines with the width of 5 to 100 μm (at intervals of 5 μm) was used as an image for a reverse thin line evaluation. For a plate life evaluation, an image suitable for plate life evaluation of solid printing was used.
After exposure in order to remove an overcoat, pre-washing with water, developing, washing with water, and plate surface treating were carried out by an automatic developing machine LP1310News (by Fujifilm Corporation). As a developing solution, a 1/4 (by water) diluted solution of a developing solution HN-D (old trade name DH-N, by Fujifilm Corporation) was used. The pH of the developing solution was 12, and the temperature of a developing bath was 30°C.
[0127] Printing was conducted by a printing press Lithron 26 (by Komori Corporation) using an ink Super Reoeco SOY Black L (by Toyo Ink Co., Ltd.), a lightweight coated paper OK Top Coat+ (by Oji Paper Co., Ltd.) and fountain solution composition. The used fountain solution composition is described below.

<Fountain solution composition>

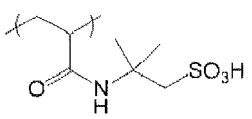
Formation of fountain solution composition before using (solution actually used)

[0128]

propylene glycol mono-*n*-butyl ether	0.5 part by mass
propylene glycol	0.5 part by mass
any of star polymers in Table 7, or B-1 comparative polymer	0.02 part by mass
carboxymethylcellulose	0.01 part by mass
ammonium nitrate	0.05 part by mass
citric acid	0.01 part by mass
malic acid	0.01 part by mass
2,2-dibromo-2-nitroethano	0.001 part by mass
benzotriazole	0.002 part by mass
2-methyl-5-chloro-4-isothiazolin-3-one	0.002 part by mass
water	add to 100 parts by mass

Comparative polymer B-1 MW=100,000

[0129]



[Evaluation]

Evaluation-1: <Evaluation of ink removal at initial start of printing>

[0130] With respect to each prepared fountain solution composition printing was carried out by a printing press Lithron 26 (by Komori Corporation) with an ink Super Reoeco SOY Black L (by Toyo Ink Co., Ltd.) and a lightweight coated paper OK Top Coat+ (by Oji Paper Co., Ltd.) and the consumed sheet number for removing ink at a non-image area at the initial start of printing was recorded (Table I). The smaller number of the consumed sheet number means better.

Evaluation-2: < Evaluation of resistance to dirt at non-image area (Evaluation of resistance to dirt after break)>

[0131] A lithographic plate original plate was subjected to forced aging at 60°C for 4 days, and then exposed and developed according to the above plate making process to obtain a lithographic plate.
The plate was mounted on a printing press (2N-600, by Tohama Seiki Co.) and printing was conducted using a ground-wood paper, an ink Soibi Red (by Inctec Inc.) and the fountain solution composition.
When the number of the printed sheets of paper used for printing reached 50, 000, the printing press was temporarily stopped and left standing for 5 hours, and then printing was restarted to print another 200 sheets. The sheet number until the ink disappeared completely from a non-image area was inspected (Table II). The smaller number means that the number of waste paper from the printing restart is fewer and therefore it is advantageous.

Evaluation-3: < Evaluation of decrease in print density by increase in total component concentration of fountain solution>

[0132] The evaluation item was evaluated by determining density decrease on a print when the total component concentration of a fountain solution composition was increased 2-, 3- and 4-fold, wherein the water scale of a printing press was changed to determine the minimum supply quantity of a fountain solution required for preventing dirt at a no-image area on a print. When the total component concentration was increased 2-, 3- and 4-fold based on the aforedescribed component concentration of a fountain solution composition, the water scale was firstly determined and then the solid image on the 500th print sheet was measured by a Macbeth densitometer (by Gretag Macbeth)
With respect to the density of a solid printed part for the 1-fold case as 100, relative densities at a solid printed part for the 2-, 3-, and 4-fold cases are shown (Table III).
Evaluation was conducted by a printing press Lithron 26 (by Komori Corporation) with an ink Super Reoeco SOY Black L (by Toyo Ink Co., Ltd.) and a lightweight coated paper OK Top Coat+ (by Oji Paper Co., Ltd.)

[0133] [Table I]

Table I: Evaluation of ink removal at initial start of printing

Example		Various polymer	Paper consumed for cleaning
Example	1	P_A-1	20
	2	P_A-2	15
	3	P_A-3	20
	4	P_A-4	15
	5	P_A-5	20
	6	P_A-6	25
Comparative example	1	B-1	65
	2	none	80

[0134] [Table II]

Table II: Evaluation of resistance to dirt at non-image area (Evaluation of resistance to dirt after break

Example		Various polymer	Paper consumed for cleaning
Example	1	P_A-1	65
	2	P_A-2	55
	3	P_A-3	50
	4	P_A-4	55
	5	P_A-5	50
	6	P_A-6	60
Comparative example	1	B-1	90
	2	none	130

[0135] [Table III]

Table III: Evaluation of decrease in print density by increase in total component concentration of fountain solution

Example		Various polymer	×1	×2	×3	×4
Example	1	P_A-1	100	100	95	95
	2	P_A-2	100	100	100	95
	3	P_A-3	100	100	95	95
	4	P_A-4	100	100	95	90
	5	P_A-5	100	95	90	90
	6	P_A-6	100	95	95	95
Comparative example	1	B-1	100	85	75	75
	2	none	100	100	95	90

[0136] As obvious from Tables I and II, when a star polymer having a hydrophilic group according to the present invention is used, compared to a case without the additive or a case in which a heretofore known water soluble polymer having sulfonic acid in a side chain, the consumed sheet number at the initial start of printing as well as at a restart of printing after a stop for a certain period can be less than a half, namely very few. It is obvious that by a fountain solution composition using a star polymer according to the invention, the dirt resistance of a non-image area at the initial start of printing as well as at a restart of printing can be improved.
Further, as obvious from Table III, even if the component concentration of a fountain solution is increased up to about 4-fold, the density of a print is substantially not decreased to demonstrate an advantageous effect.

[Examples 7 to 33 and Comparative Examples 3 to 4]

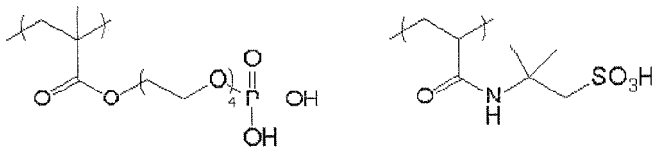
[0137] A thermal negative-type digital plate was prepared identically with Example 1 and plate making was carried out. Printing was carried out by a printing press Lithron 26 (by Komori Corporation) using an ink Super Reoeco SOY Black L (by Toyo Ink Co., Ltd.), a lightweight coated paper OK Top Coat+ (by Oji Paper Co., Ltd.), and a fountain solution composition. The used fountain solution composition is described below.

<Fountain solution composition>

[0138]

Formation of fountain solution composition before using (solution actually used)	
propylene glycol mono-*n*-butyl ether	0.5 part by mass
propylene glycol	0.5 part by mass
any of star polymers in Tables 8 to 12, or PN-1 comparative polymer shown below	0.2 part by mass
carboxymethylcellulose	0.01 part by mass
ammonium nitrate	0.05 part by mass
citric acid	0.01 part by mass
malic acid	0.01 part by mass
2,2-dibromo-2-nitroethano	0.001 part by mass
benzotriazole	0.002 part by mass
2-methyl-5-chloro-4-isothiazolin-3-one	0.002 part by mass
water	add to 100 parts by mass

[0139]



20/80

Comparative polymer PN-1

Mw=110000

[0140] Evaluation-1 to Evaluation-3 were conducted with respect to each fountain solution identically with Example 1. The results are shown in Tables IV to VI.

[0141] [Table IV]

Table IV: Evaluation of ink removal at initial start of printing

Example		Various polymer	Paper consumed for cleaning
Example	7	P_{AB}-1	15
	8	P_{AB}-2	10
	9	P_{AB}-3	25
	10	PA_{B}-4	20
	11	P_{AB}-5	15
	12	P_{AB}-6	20
	13	P_{AB}-7	15
	14	P_{AB}-8	20
	15	P_{AB}-9	25
	16	P_{AB}-10	35
	17	P_{AB}-11	25
	18	P_{AB}-12	15
	19	P_{AS}-13	20
	20	P_{AB}-14	25
	21	P_{AB}-15	25
	22	P_{AB}-16	20

(continued)

Example		Various polymer	Paper consumed for cleaning
	23	P_{AB}-17	25
	24	P_{AB}-18	20
	25	P_{AB}-19	25
	26	P_{AB}-20	35
	27	P_{AB}-21	20
	28	P_{AB}-22	15
	29	P_{AB}-23	15
	30	P_{AB}-24	20
	31	P_{AB}-25	15
	32	P_{AB}-26	15
	33	P_{AB}-27	20
Comparative example	3	PN-1	60
	4	none	80

[0142] [Table V]

Table V: Evaluation of resistance to dirt at non-image area (Evaluation of resistance to dirt after break

Example		star polymer	dirt (number)
Example	7	P_{AB}-1	25
	8	P_{AB}-2	30
	9	P_{AB}-3	25
	10	P_{AB}-4	30
	11	P_{AB}-5	35
	12	P_{AB}-6	30
	13	P_{AB}-7	35
	14	P_{AB}-8	30
	15	P_{AB}-9	35
	16	P_{AB}-10	45
	17	P_{AB}-11	35
	18	P_{AB}-12	35
	19	P_{AB}-13	40
	20	P_{AB}-14	45
	21	P_{AB}-15	45
	22	P_{AB}-16	40
	23	P_{AB}-17	45
	24	P_{AB}-18	40
	25	P_{AB}-19	45
	26	P_{AB}-20	50
	27	P_{AB}-21	30

(continued)

Example		star polymer	dirt (number)
	28	P_{AB}-22	25
	29	P_{AB}-23	25
	30	P_{AB}-24	30
	31	P_{AB}-25	25
	32	P_{AB}-26	25
	33	P_{AB}-27	30
Comparative example	3	PN-1	70
	4	none	130

[0143] [Table VI]

Table VI: Evaluation of decrease in print density by increase in total component concentration of fountain solution

Example		Various polymer	×1	×2	×3	×4
Example	1	P_{AB}-1	100	95	95	90
	2	P_{AB}-2	100	100	95	95
	3	P_{AB}-3	100	100	95	95
	4	P_{AB}-4	100	90	90	85
	5	P_{AB}-5	100	95	95	95
	6	P_{AB}-6	100	95	95	90
	7	P_{AB}-7	100	100	95	90
	8	P_{AB}-8	100	95	95	90
	9	P_{AB}-9	100	90	85	85
	10	P_{AB}-10	100	90	90	90
	11	P_{AB}-11	100	95	95	90
	12	P_{AB}-12	100	95	95	95
	13	P_{AB}-13	100	95	90	85
	14	P_{AB}-14	100	100	95	95
	15	P_{AB}-15	100	95	90	90
	16	P_{AB}-16	100	90	90	85
	17	P_{AB}-17	100	90	90	90
	18	P_{AB}-18	100	95	90	85
	19	P_{AB}-19	100	95	95	90
	20	P_{AB}-20	100	100	100	95
	21	P_{AB}-21	100	90	90	85
	22	P_{AB}-22	100	95	90	85
	23	P_{AB}-23	100	100	95	95
	24	P_{AB}-24	100	100	100	95
	25	P_{AB}-25	100	100	100	100
	26	P_{AB}-26	100	95	90	85

(continued)

Example	Various polymer	×1	×2	×3	×4
27	P_{AB}-27	100	95	95	90
Comparative example 1	PN-1	100	85	75	70
2	none	100	100	95	90

[0144] As obvious from Tables IV and V, when a star polymer having a hydrophilic group and a substrate adsorptive group according to the present invention is used, compared to a case without the additive or a case in which a conventional polymer having a phosphate group and sulfonic acid in a side chain, the consumed sheet number at the initial start of printing as well as at a restart of printing after a stop for a certain period can be less than a half, namely very few. It is obvious that by a fountain solution composition using a star polymer according to the invention, the dirt resistance of a non-image area at the initial start of printing as well as at a restart of printing can be improved.
Further, as obvious from Table VI, even if the component concentration of a fountain solution is increased up to about 4-fold, the density of a print is substantially not decreased to demonstrate an advantageous effect.

Claims

1. A fountain solution composition for lithographic printing **characterized by** comprising a star polymer having at least one hydrophilic group.

2. The fountain solution composition for lithographic printing according to claim 1, wherein the star polymer is a star polymer having 3 branches to 10 branches (both inclusive).

3. The fountain solution composition for lithographic printing according to claim 1 or 2, wherein the star polymer has 3 branches to 10 branches (both inclusive) of polymer chains branched from a skeleton through sulfide bonds.

4. The fountain solution composition for lithographic printing according to claim 3, wherein the star polymer has 3 branches to 10 branches (both inclusive) of polymer chains branched from a skeleton through sulfide bonds, the polymer being obtained by polymerizing an ethylenic unsaturated monomer in the presence of a multifunctional thiol.

5. The fountain solution composition for lithographic printing according to any one of claims 1 to 4, **characterized in that** the star polymer further comprises at least one substrate adsorptive group.

6. The fountain solution composition for lithographic printing according to claim 5, wherein the substrate adsorptive group of the star polymer is at least one selected from the group consisting of a phosphonic acid group and a salt thereof, a phosphoric ester group and a salt thereof, and a carboxylic acid group and a salt thereof.

7. The fountain solution composition for lithographic printing according to any one of claims 1 to 6, wherein the hydrophilic group of the star polymer is at least one selected from the group consisting of a sulfonic acid group and a salt thereof, an amide group, a polyalkylene oxide group, a hydroxy group, a sulfuric monoester group and a salt thereof, a sulfonamide group, an amino group, a sulfuric acid-monoamide group and a salt thereof, and a betaine structure.

8. The fountain solution composition for lithographic printing according to any one of claims 1 to 7 comprising a water soluble polymer not having a star structure.

9. The fountain solution composition for lithographic printing according to claim 8, wherein the water soluble polymer not having a star structure is at least one water soluble macromolecular compound selected from the group consisting of gum arabic, a cellulose derivative and a modification thereof, polyvinyl alcohol and a derivative thereof, polyvinylpyrrolidone, a vinyl methyl ether/maleic anhydride copolymer, a vinyl acetate/maleic anhydride copolymer, a styrene/maleic anhydride copolymer, a water soluble soybean polysaccharides, starch, a starch derivative, pullulan and a pullulan derivative, gelatin, and hemicellulose extracted from a soybean.

10. The fountain solution composition for lithographic printing according to any one of claims 1 to 9 which is a concentrated

fountain solution composition.

REFERENCES CITED IN THE DESCRIPTION

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