

11

METHOD OF CLEANING SUPPORTS USED IN PRINTING

The present invention relates to a method of cleaning supports used in printing.

Supports used in printing such as screen meshes to be fitted with photosensitive resin films to form printing bases tends to become stained with dirt such as human sebum, oil and dust. When such a stained screen mesh is fitted with a photosensitive resin film, uneven printing results and a clear print cannot be obtained.

Dirt has been removed heretofore with a neutral detergent as disclosed in the specification of Japanese Patent Publication No. 38506/1977.

However, even though dirt can be removed with such a neutral detergent, the screen mesh is poorly wettable with water and, therefore, it cannot be fitted exactly with the photosensitive resin film.

Further, though the screen mesh has been cleaned with a detergent containing an organic acid to exhibit excellent washability and wettability with water, the

detergent must be used carefully because the organic acid is strong acid.

We have found that the deterging power and water retention of a treating agent for printing bases can be improved remarkably by incorporating a cationic polymer and an anionic surfactant therein to form a complex and to increase the absorbability thereof onto a screen mesh.

According to this invention we therefore provide a method of cleaning a support used in printing such as a print master which comprises treating the support with a composition comprising 0.1 to 15 percent by weight of a cationic polymer, 0.1 to 15 percent by weight of an anionic surfactant and water.

It is preferable that the composition further comprises 0.5 to 10 percent by weight of a nonionic surfactant. Alternatively it preferably comprises 0.1 to 10 percent by weight of a nonionic surfactant and 0.001 to 5 percent by weight of a polymer of maleic acid or maleic

3

3

anhydride, a copolymer thereof or a water-soluble salt of the polymer or copolymer.

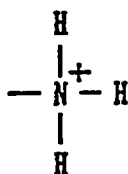
A preferred composition for use in the invention ~~which~~ contains a cationic polymer, _____

an anionic surfactant, a nonionic surfactant and a homopolymer of maleic acid or maleic anhydride, a copolymer thereof with a monomer copolymerizable therewith or a water-soluble salt of said polymer.

By means of the present invention dirt can be _____ thoroughly removed from a printing _____ screen mesh and its wettability by water can be improved. Therefore, the screen mesh can be fitted exactly with a photosensitive film and, as a result, evenly printed products can be obtained. Another advantage is that the treating agent used in the invention can be used safely, since it is neutral.

The cationic polymer used in the present invention may be any of those having the following functional groups:

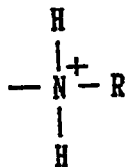
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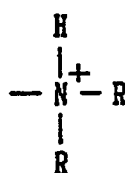
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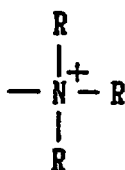
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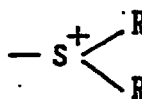
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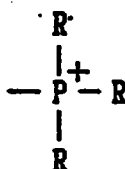
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No. 5



No. 6

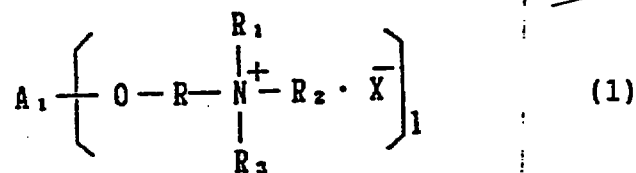


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5

Of the above, quaternary salts (No. 4) are particularly preferred.

Preferred examples of the cationic polymers used in the present invention include cationic starches and cationic celluloses of the following general formula (1):



wherein A_1 represents a starch or cellulose residue, R represents an alkylene or hydroxyalkylene group, R_1 , R_2 and R_3 may be the same or different and represent each an alkyl, aryl or aralkyl group or they may form a heterocyclic ring including the nitrogen atom contained in the above formula, X represents an anion such as chlorine, bromine, iodine or sulfate, sulfonate, methylsulfate, phosphate or nitrate ion, and 1 represents a positive integer.

The cationic starch can be obtained by, for example, reacting starch with glycidyltrimethylammonium chloride or 3-chloro-2-hydroxypropyltrimethylammonium chloride under alkaline conditions. Another process

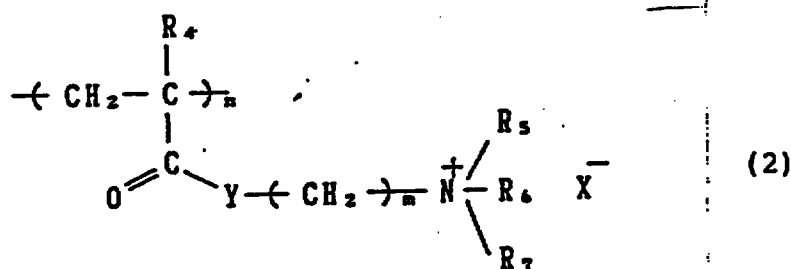
for obtaining the cationic starch comprises quaternizing dimethylaminoethylated starch. Still another process comprises reacting starch with 4-chlorobutenyltrimethylammonium chloride.

The cationic cellulose can be obtained by, for example, subjecting hydroxyethylcellulose to the above-mentioned reaction.

The degree of substitution of the cationic starch or cationic cellulose with the cations is 0.01 to 1. Thus, those containing 0.01 to 1, preferably 0.02 to 0.5, cation group per anhydrous glucose unit are used.

The cationic polymer is contained in the treating agent in an amount of 0.1 to 15 wt. %, preferably 1 to 10 wt. %.

The cationic polymers used in the present invention include also cationic vinyl polymers of the following formulae (2), (3), (4) and (5):

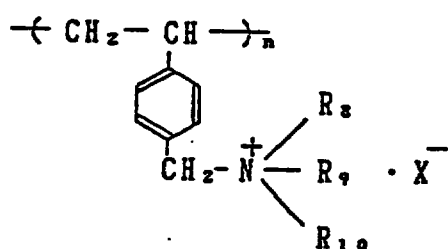


wherein R_4 represents a hydrogen atom or a methyl group, R_5 , R_6 and R_7 may be the same

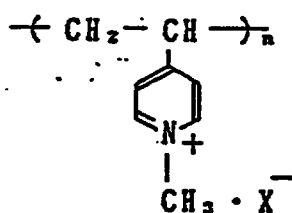
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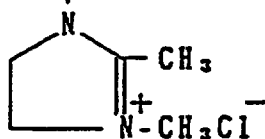
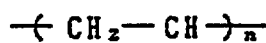
or different and represent each a hydrogen atom or a substituted or unsubstituted alkyl group having 1 to 4 carbon atoms, Y represents an oxygen atom or an NH group in an amide bond, X is as defined in the above formula (1), and m represents an integer of 1 to 10,



wherein R₈, R₉ and R₁₀ may be the same or different and represent each a hydrogen atom or a substituted or unsubstituted alkyl group having 1 or 2 carbon atoms and X is as defined in the above formula (1)



wherein X is as defined in the above formula (1),



(5)

poly(N-vinyl-2,3-dimethylimidazolinium
chloride)

These cationic vinyl polymers may be used either alone or in the form of a mixture of two or more of them in the present invention.

The anionic surfactants used in the invention include the following ones:

- 1) straight-chain or branched alkylbenzenesulfonates having an alkyl group having 10 to 16 carbon atoms on average,
- 2) alkyl or alkenyl ether sulfates having a straight-chain or branched alkyl or alkenyl group having 10 to 20 carbon atoms on average, to which is added 0.5 to 8 mol on average of ethylene oxide, propylene oxide or butylene oxide or both ethylene oxide and propylene oxide in a ratio of 0.1/9.9 to 9.9/0.1 or both ethylene oxide and butylene oxide in a ratio of 0.1/9.9 to 9.9/0.1,
- 3) salts of alkyl or alkenyl sulfates having an alkyl



or alkenyl group having 10 to 20 carbon atoms on average,

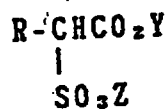
4) olefinsulfonates having 10 to 20 carbon atoms on average in the molecule,

5) alkanesulfonates having 10 to 20 carbon atoms on average in the molecule,

6) saturated or unsaturated fatty acid salts having 10 to 24 carbon atoms on average in the molecule,

7) salts of alkyl or alkenyl ether carboxylates having an alkyl or alkenyl group having 10 to 20 carbon atoms on average, to which is added 0.5 to 8 mol on average of ethylene oxide, propylene oxide or butylene oxide or both ethylene oxide and propylene oxide in a ratio of 0.1/9.9 to 9.9/0.1 or both ethylene oxide and butylene oxide in a ratio of 0.1/9.9 to 9.9/0.1.

8) α -sulfo fatty acid salts or esters of the following formula:



wherein Y represents an alkyl group having 1 to 3 carbon atoms or a counter ion, Z represents a counter ion and R represents an

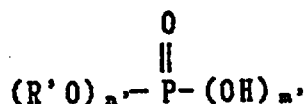
alkyl or alkenyl group having 10 to 20
carbon atoms,

9) alkyl or alkenylsuccinic acid salts having 10 to 22
carbon atoms on average.

The counter ions of the above-mentioned anionic
surfactants include alkali metal ions such as sodium
and potassium ions; alkaline earth metal ions such as
calcium and magnesium ions; ammonium ion; and alkanol-
amines having 1 to 3 alkanol groups each having 2 or
3 carbon atoms.

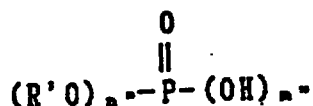
10) the following phosphoric ester surfactants:

No. 1: acid alkyl (or alkenyl) phosphates:



wherein R' represents an alkyl or alkenyl
group having 8 to 24 carbon atoms, $n'+m'$ is
3 and n' is 1 to 2,

No. 2: alkyl (or alkenyl) phosphates:

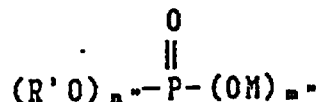


wherein R' is as defined above, $n''+m''$ is 3
and n'' is 1 to 3, and

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No. 3: salts of alkyl (or alkenyl) phosphates:



wherein R', n" and m" are as defined above
and M represents Na, K or Ca.

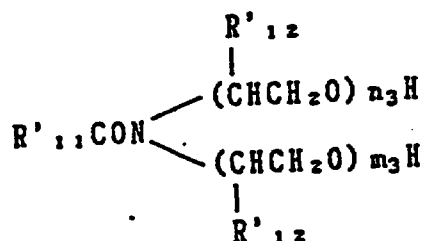
Among the above compounds, those having a high complex-forming power are preferred. Particularly preferred are sodium salts of the above-mentioned alkylbenzenesulfonic acids(1).

The anionic surfactants are used in an amount of preferably 0.1 to 15 wt. %, particularly 1 to 10 wt. %.

The nonionic surfactants used in the present invention include the following ones:

- 1) polyoxyethylene alkyl or alkenyl ethers having an alkyl or alkenyl group having 10 to 20 carbon atoms on average, to which is added 1 to 20 mol of ethylene oxide,
- 2) polyoxyethylene alkylphenyl ethers having an alkyl group having 6 to 12 carbon atoms on average, to which is added 1 to 20 mol of ethylene oxide,
- 3) polyoxypropylene alkyl or alkenyl ethers having an alkyl or alkenyl group having 10 to 20 carbon atoms on average, to which is added 1 to 20 mol of propylene oxide.

- 4) polyoxybutylene alkyl or alkenyl ethers having an alkyl or alkenyl group having 10 to 20 carbon atoms on average, to which is added 1 to 20 mol of butylene oxide,
- 5) nonionic surfactants having an alkyl or alkenyl group having 10 to 20 carbon atoms on average, to which is added 1 to 30 mol, in total, of ethylene oxide and propylene oxide or butylene oxide (the ratio of ethylene oxide to propylene oxide or butylene oxide: 0.1/9.9 to 9.9/0.1),
- 6) higher fatty acid alkanolamides of the following general formula and alkylene oxide adducts thereof:



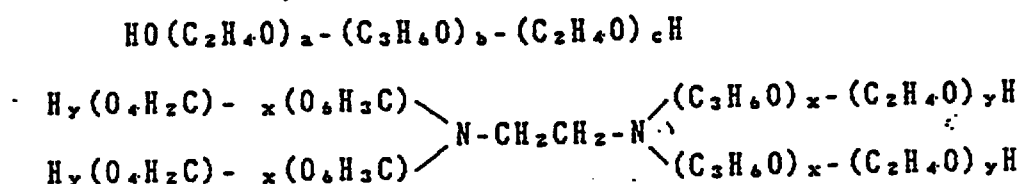
wherein R'_{11} represents an alkyl or alkenyl group having 10 to 20 carbon atoms, R'_{12} represents H or CH_3 , n_3 represents an integer of 1 to 3 and m_3 represents an integer or

0 to 3,

- 7) sucrose/fatty acid esters comprising a fatty acid having 10 to 20 carbon atoms on average and sucrose,

8) glycerol monoesters of fatty acids comprising a fatty acid having 10 to 20 carbon atoms on average and glycerol, and

9) polyoxyethylene polyoxypropylene block copolymer surfactants of the following general formulae:



wherein a, b and c represent each an integer of 2 to 20 and x and y represent each an integer of 2 to 20.

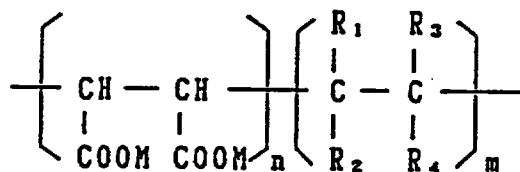
Among the above-mentioned nonionic surfactants, those having a high affinity for the complex are preferred. Particularly, polyoxyethylene alkyl or alkenyl ethers

(1) are preferred.

The nonionic surfactant is used in an amount of 0.5 to 10 wt. %, preferably 1 to 8 wt. %.

Among the homopolymers of maleic acid or maleic anhydride, the copolymers thereof with monomers copolymerizable therewith and the water-soluble salts of these polymers used in the present invention, the most preferred are homopolymers, copolymers and

their salts having a molecular weight of about 1,000 to 100,000 and represented by the following general formula:



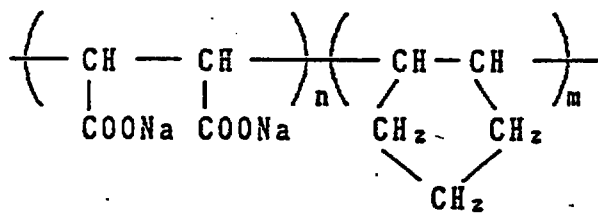
wherein R_1 , R_2 , R_3 and R_4 represent each a hydrogen atom or a substituted or unsubstituted alkyl group (R_1 and R_3 may form together a cycloalkyl ring), carboxyl group or alkoxyl group having 1 to 3 carbon atoms, M represents a hydrogen atom, an alkali metal or an alkanolamine group and n and m represent each 0 or a positive number, n/m being 1/10 to 1/30.

The above general formula represents not block copolymers but copolymers including random copolymers (and homopolymers when m is 0).

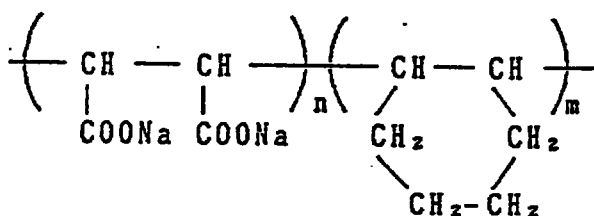
Examples of the above-mentioned copolymers include the following ones:

26

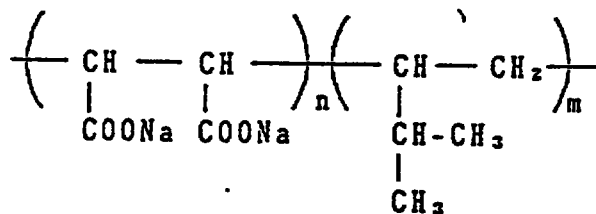
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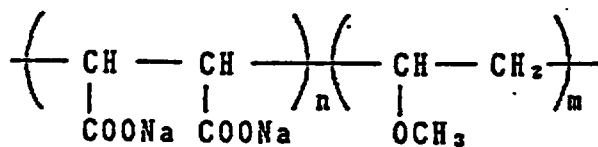
$n/m=1/1$, M.W.; about 6,000



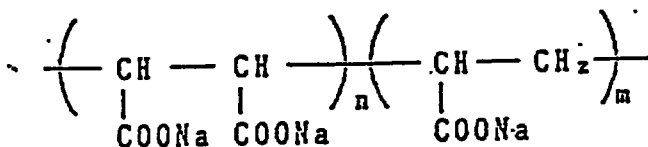
$n/m=1/1$, M.W.; about 4,000



$n/m=1/1$, M.W.; about 5,000



$n/m=1/1$, M.W.; about 10,000



$n/m=1/20$, M.W.; about 15,000

Among them, particularly preferred are copolymers of cyclopentene and cyclohexene. They are used in an amount of 0.001 to 5 wt. %, preferably 0.05 to 1 wt. %.

The treating agent used in the invention may further contain thickening agent, pigment, colorant, flavor, germicide, antiseptic, etc., if desired.

The balance comprises water or a mixture of water and a water-soluble solvent.

Examples of the water-soluble solvents include lower alcohols such as methanol, ethanol, propanol, isopropanol and butanol; carbitols such as butylmono-, -di- or -triglycols; cellosolves such as methyl cellosolve and ethyl cellosolve; and acetone.



The present invention will now be illustrated with reference to the following non-limiting examples.

In tables given below, all percentages are in terms of wt. % except for the "deterging rate", which is explained hereinafter.

Examples 1 to 3 and Comparative Examples 1 and 2

The deterging powers and wettability with water of the compositions shown in Table 1 were examined to obtain the results shown in Table 1.

Method of deterging power test:

A rape seed oil was applied uniformly to the surface of a polyester screen mesh. The screen mesh was rubbed with a sponge impregnated with 5 g of a detergent (5 back and forth strokes), washed with water and dried. The deterging power was represented in terms of the "deterging rate" calculated as follows:

D (deterging rate: %)

$$= \frac{\text{weight of rape seed oil after deterging (g)}}{\text{weight of rape seed oil before deterging (g)}} \times 100$$

Method of water wettability test:

The polyester screen mesh deterged as mentioned above was immersed in water and pulled up gently to determine the wettability thereof by water according



to the following criteria:

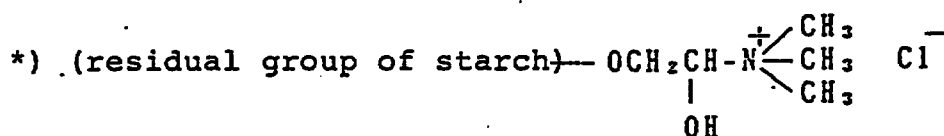
○ : complete wetting

Δ : water was repelled partially, and

X : water was repelled entirely.

Table 1

Composition	Comp. Exs.		Examples		
	1	2	1	2	3
Cationic starch*	5	-	5	1	2
Sodium alkyl(C ₁₂)benzene-sulfonate	-	5	5	1	2
Sodium alkyl(C ₁₂) sulfate	-	-	-	-	2
Tap water	95	95	90	98	94
Deterging rate (%)	31	65	83	80	78
Wettability with water	X	X	○	○	○ ~ Δ



Examples 4 and 5 and Comparative Example 3

The deterging powers and wettabilities with water of the compositions shown in Table 2 were examined to obtain the results shown in Table 2.

Table 2

Composition	Comp. Exs.	Examples	
	3	4	5
Cationic starch*	5	5	5
Sodium alkyl(C ₁₂)benzene-sulfonate	-	5	5
Polyoxyethylene alkyl ether**	5	-	3
Tap water	90	90	87
Deterging rate (%)	72	83	96
Wettability with water	X	○	○

*) see Table 1,

**) C₁₂, EO=8.

Examples 6 and 7 and Comparative Examples 4 and 5

Deterging power and wettability with water of each composition shown in Table 3 were examined and results are shown in Table 3.

Method of antiredeposition effect test

400 cc of tap water and 0.1 g of carbon black were placed in a 500 cc beaker and stirred with a magnetic stirrer. The deterged polyester screen mesh was immersed therein and then pulled up gently and the antiredeposition effect thereof was determined

(31)

21

Examples 8 and 9 and Comparative Examples 6 and 7

Each composition shown in Table 4 was examined in respect to deterging power, wettability with water and antiredeposition effect and results are shown in Table 4.

Table 4

Composition	Comp. Exs.		Examples	
	6	7	8	9
Cationic starch*1	5	5	5	5
Sodium alkyl(C ₁₂)benzenesulfonate			5	5
Polyoxyethylene alkyl ether*2	10			3
Polyoxyethylene nonylphenol (C ₉ ; EO=12)			5	
Cyclopentene/anhydrous Na maleate (1:1) (MW=6000)		1	0.1	0.5
Tap water	85	94	84.9	86.5
Deterging rate (%)	73	70	94	97
Wettability with water	X	X	○	○
Antiredeposition effect	X	X	○	○

*1: see Table 3

*2: see Table 3



CLAIMS:

1. A method of cleaning a support used in printing such as a print master which comprises treating the support with a composition comprising 0.1 to 15 percent by weight of a cationic polymer, 0.1 to 15 percent by weight of an anionic surfactant and water.
2. A method as claimed in Claim 1, in which the composition further comprises 0.5 to 10 percent by weight of a nonionic surfactant.
3. A method according to Claim 1 in which the composition further comprises 0.1 to 10 percent by weight of a nonionic surfactant and 0.001 to 5 percent by weight of a polymer of maleic acid or maleic anhydride, a copolymer thereof or a water-soluble salt of such a polymer or copolymer.
4. A method according to Claim 1 in which said cationic polymer is selected from a cationic starch a cationic cellulose and cationic vinyl polymer.