(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 638 436 A1**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **94112430.7**

(51) Int. Cl.[6]: **B41N 3/08**

(22) Date of filing: **09.08.94**

(30) Priority: **12.08.93 JP 200751/93**

(43) Date of publication of application:
15.02.95 Bulletin 95/07

(84) Designated Contracting States:
DE GB

(71) Applicant: **FUJI PHOTO FILM CO., LTD.**
210 Nakanuma
Minami-Ashigara-shi
Kanagawa (JP)

(72) Inventor: **Matsumoto, Hiroshi, c/o Fuji Photo Film Co., Ltd.**
4000, Kawashiri,
Yoshida-cho
Haibara-gun,
Shizuoka (JP)
Inventor: **Kunichika, Kenji, c/o Fuji Photo Film Co., Ltd.**
4000, Kawashiri,
Yoshida-cho
Haibara-gun,
Shizuoka (JP)

(74) Representative: **Patentanwälte Grünecker, Kinkeldey, Stockmair & Partner**
Maximilianstrasse 58
D-80538 München (DE)

(54) **Surface protective agent and cleaning agent for lithographic printing plate.**

(57) A surface protective agent for a lithographic printing plate, comprising an aqueous solution containing a film-forming water-soluble soybean polysaccharide, and an emulsion type plate cleaning agent comprising a film-forming polysaccharide extracted from soybean.

EP 0 638 436 A1

FIELD OF THE INVENTION

The present invention relates to a surface protective agent for a lithographic printing plate and to a cleaning agent for a lithographic printing plate.

BACKGROUND OF THE INVENTION

In the process for the preparation of a lithographic printing plate, the material is coated with a so-called gum solution at the final stage thereof.

The object of coating with a gum solution is to protect the water wettability of the non-image area as well as to inhibit the contamination of the printing plate due to the attachment of scumming such as fingerprints, fats and oils and dust, and protect the printing plate against the occurrence of scratches during image correction such as addition and deletion on the image area, storage between plate making and printing or reuse, mounting on a printing machine, or in handling. Further, the object of coating with a gum solution is to inhibit the occurrence of oxidative contamination. As the gum solution for a lithographic printing plate, an aqueous solution of gum arabic, cellulose gum or water-soluble high molecular substance having carboxyl groups in its molecule has heretofore been normally used. However, such a gum solution has some disadvantages. In some detail, the final finishing process in the preparation of a printing plate is normally carried out by pouring a gum solution onto the printing plate, spreading the gum solution over the entire surface of the printing plate with a sponge, cotton tampon or the like, and then rubbing the surface of the printing plate with the sponge, cotton tampon or the like until it is dried. As a result, the image area (ink-receptive area) is partly coated thickly with a water-soluble high molecular substance. The thickly coated image area exhibits a reduced ink-receptivity during printing. Thus, a considerable number of sheets of paper must be wasted until a printed matter having a desired ink density can be obtained. In general, this phenomenon is called printing fault (so-called poor ink-receptivity). In order to recover the lost image area against the foregoing difficulty, a process is normally required which comprises washing the printing plate with water or a weakly acidic solution to remove a hydrophilic colloid from the image area. Since this washing process requires much time, a gum remover has been developed as disclosed in JP-B-56-19277 (the term "JP-B" as used herein means an "examined Japanese patent publication").

On the other hand, it is a common practice to cover the image area with fats and oils before gumming to maintain the ink-receptivity of the image area. However, this practice is undesirable because it complicates the procedure and reduces the working efficiency as well as causes an environmental pollution with waste and injures workers' health. Accordingly, attempts have been made to use a water-soluble organic high molecular compound which causes no printing fault as a surface protective agent. For example, JP-A-52-56603 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-54-97102, West German Patent 2,504,594, and Soviet Patent 623,755 propose dextrin, pullulan, pullulan derivatives, carboxyl-containing polyacrylamide derivatives, and methyl (meth)-acrylate graft polyacrylamide copolymer. Further, modified starch compounds such as carboxymethylated modified starch and cyclodextrin are disclosed. Since these compounds have an insufficient effect of desensitizing the non-image area, they are used in admixture with gum arabic. Further, since these compounds have an unstable adaptability to protective colloid of emulsion as compared with gum arabic, the use thereof is limited.

On the other hand, it is a common practice that a lithographic printing plate which has suffered from scumming is treated with a so-called plate cleaning agent (also referred to as "plate cleaner") for removing ink from the plate as well as recovering the hydrophilicity of the non-image area. As one such plate cleaning agent there has heretofore been known one comprising an aqueous solution of sodium silicate. However, this plate cleaning agent is disadvantageous in that it is alkaline and thus can attack part of the image area or deteriorate the ink affinity of the image area when used to treat a photosensitive lithographic printing plate adapted to be developed with an aqueous alkaline developer.

In general, when summing occurs during printing, the printing plate is treated with a cleaning agent (kerosine or hydrocarbon solvent) to remove an ink therefrom, and then treated with a desensitizing agent. The treatment with the conventional plate cleaning agents as mentioned above must be conducted after the cleaning of the plate with an ink remover. Thus, the treatment with these plate cleaning agents requires two steps and thus is complicated. In order to eliminate these difficulties, an emulsion type plate cleaning agent, i.e., plate cleaning agent which can exert an ink removing effect as well as desensitizing effect has been recently developed. For example, JP-A-52-15702 discloses an alkaline emulsion type plate cleaning agent, and JP-A-53-2102 discloses an acidic emulsion type plate cleaning agent.

However, these emulsion type plate cleaning agents are disadvantageous in that they have a poor capacity of removing scumming caused by scratching from a lithographic printing plate which has been subjected to a burning-in treatment or cannot exert an effect of desensitizing the scratched area for a sufficient period of time, causing occasional recurrence of scumming during printing.

The foregoing acidic emulsion type plate cleaning agent normally comprises much gum arabic as a protective colloid component for stabilizing emulsion to utilize its inherent effect of inhibiting scumming on the non-image area. On the other hand, the foregoing alkaline emulsion type plate cleaning agent normally comprises a cellulose high molecular compound instead of gum arabic because gum arabic undergoes gelation in the alkaline emulsion type plate cleaning agent. Accordingly, the alkaline emulsion type plate cleaning agent is disadvantageous in that it suffers from unstable emulsification that leads to separation of liquid and thus can cause uneven treatment unless it is thoroughly stirred and homogenized before use after prolonged storage.

On the other hand, gum arabic is mainly produced in the Sudan, which is called a gum arabic belt in the African Continent. In recent years, however, a drought due to climatic change and a political instability have caused a marked market change that makes the product hardly available. Thus, the development of alternate high molecular compounds has been desired.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a surface protective agent which desensitizes the non-image area on a lithographic printing plate as well as causes no printing faults even after a prolonged storage.

Another object of the present invention is to provide a surface protective agent which can be easily applied onto the surface of a lithographic printing plate with a sponge, cotton tampon, automatic gum coater or the like, can be easily removed water wettability of the non-image area and can be used without gum arabic.

Still another object of the present invention is to provide a plate cleaning agent for a lithographic printing plate having an excellent capacity of removing scumming as well as a high aging stability.

The foregoing objects of the present invention will become more apparent from the following detailed description and examples.

In order to accomplish the foregoing objects of the present invention, the inventors made extensive studies. As a result, the inventors have worked out the present invention.

These and other objects of the present invention have been achieved by a surface protective agent for a lithographic printing plate, comprising an aqueous solution containing a film-forming water-soluble soybean polysaccharide.

Further, these and other objects of the present invention have been achieved by an emulsion type plate cleaning agent comprising a film-forming polysaccharide extracted from soybean.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be further described hereinafter.

A water-soluble soybean polysaccharide is extracted from soybean with water, and mainly comprises galactose, arabinose and galacturonic acid. It is commercially available as Soyafive-S-LN from FUJI OIL COMPANY, LIMITED.

The soybean polysaccharide used in the present invention has preferably an average molecular weight of from 50,000 to 1,000,000 and a viscosity of from 5 to 100 cp (centipoises) in a 10% by weight aqueous solution at a temperature of 25 °C.

The content of such a soybean polysaccharide in the surface protective agent according to the present invention is preferably from 0.3 to 50% by weight, more preferably from 0.5 to 40% by weight. Such a soybean polysaccharide is used in the form of homogeneous solution in water or hot water. In the present invention, such a soybean polysaccharide is used in combination with one or more starches or modified starches such as dextrin.

Further, such a soybean polysaccharide may be used in combination with one or more water-soluble high molecular compounds. Examples of these water-soluble high molecular compounds include gum arabic, cellulose derivatives (e.g., carboxymethyl cellulose, carboxyethyl cellulose, methyl cellulose) and modified compounds thereof, polyvinyl alcohol and derivatives thereof, polyvinyl pyrrolidone, polyacrylamide and copolymers thereof, vinyl methyl ether-maleic anhydride copolymer, vinyl acetate-maleic anhydride copolymer and styrene-maleic anhydride copolymer.

The surface protective agent according to the present invention is usually used to advantage in an acidic range of pH 3 to 6. In order to make pH 3 to 6, the surface protective agent is usually adjusted with a mineral acid, an organic acid or an inorganic salt in an amount of from 0.01 to 2% by weight. Examples of the mineral acid include nitric acid, sulfuric acid, phosphoric acid and metaphosphoric acid. Examples of the organic acid include citric acid, acetic acid, oxalic acid, malonic acid, p-toluenesulfonic acid, tartaric acid, malic acid, lactic acid, levulinic acid, phytic acid and organic phosphonic acid. Examples of the inorganic salt include magnesium nitrate, monobasic sodium phosphate, dibasic sodium phosphate, nickel sulfate, sodium hexametaphosphate and sodium tripolyphosphate. The mineral acid, organic acid or inorganic salt may be used singly or in combination with one or more thereof.

The surface protective agent according to the present invention may comprise a surface active agent incorporated therein to improve the surface properties of the coated layer. Examples of the surface active agent used in the present invention include an anionic surface active agent and/or nonionic surface active agent.

Examples of the anionic surface active agent include aliphates, abietates, hydroxyalkanesulfonates, alkanesulfonates, dialkylsulfosuccinates, straight-chain alkylbenzenesulfonates, branched alkylbenzenesulfonates, alkylnaphthalenesulfonates, alkylphenoxypolyoxyethylenepropylsulfonates, salts of polyoxyethylene alkylsulfophenyl ethers, sodium N-methyl-N-oleyltaurates, monoamide disodium N-alkylsulfosuccinates, petroleum sulfonates, sulfated castor oil, sulfated tallow oil, salts of sulfuric esters of aliphatic alkylesters, salts of alkylsulfuric esters, sulfuric esters of polyoxyethylenealkylethers, salts of sulfuric esters of aliphatic monoglycerides, salts of sulfuric esters of polyoxyethylenealkylphenylethers, salts of sulfuric esters of polyoxyethylenestyrylphenylethers, salts of alkylphosphoric esters, salts of phosphoric esters of polyoxyethylenealkylethers, salts of phosphoric esters of polyoxyethylenealkylphenylethers, partially saponified compounds of styrenemaleic anhydride copolymers, partially saponified compounds of olefin-maleic anhydride copolymers, and naphthalenesulfonateformalin condensates. Particularly preferred among these anionic surface active agents are dialkylsulfosuccinates, salts of alkylsulfuric esters and alkylnaphthalenesulfonates.

Examples of the nonionic surface active agent include polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, polyoxyethylene polystyryl phenyl ethers, polyoxyethylene polyoxypropylene alkyl ethers, polyoxyethylene polyoxypropylene block polymers, partial esters of glycerinaliphatic acids, partial esters of sorbitanaliphatic acid, partial esters of pentaerythritolaliphatic acid, propyleneglycolmonoaliphatic esters, partial esters of sucrosealiphatic acids, partial esters of polyoxyethylenesorbitanaliphatic acid, partial esters of polyoxyethylenesorbitolaliphatic acids, polyethyleneglycolaliphatic esters, partial esters of polyglycerinaliphatic acids, polyoxyethylenated castor oils, partial esters of polyoxyethyleneglycerinaliphatic acids, aliphatic diethanolamides, N,N-bis-2-hydroxyalkylamines, polyoxyethylene alkylamines, triethanolaminealiphatic esters, and trialkylamine oxides. Particularly preferred among these nonionic surface active agents are polyoxyethylene alkylphenyl ethers and poloxyethylene-polyoxypropylene block polymers.

Further, fluorinic and siliconic anionic and nonionic surface active agents may be similarly used.

Two or more of these surface active agents may be used in combination. For example, a combination of two or more different anionic surface active agents or a combination of an anionic surface active agent and a nonionic surface active agent is preferred.

The amount of such a surface active agent to be used is not specifically limited but is preferably from 0.01 to 20% by weight based on the weight of the surface protective agent.

Besides the foregoing components, a wetting agent such as ethylene glycol, propylene glycol, triethylene glycol, butylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol, glycerin, trimethylol propane and diglycerin may be used if desired. The wetting agent may be used singly or in combination with one or more thereof. In general, the foregoing wetting agent is preferably used in an amount of from 1 to 25% by weight based on the weight of the surface protective agent.

Further, a chelate compound may be added to the surface protective agent according to the present invention.

A surface protective agent is normally available in the form of concentrated solution. The surface protective agent is diluted with tap water, well water or the like before use. Calcium ion and other impurities contained in the diluting tap water or well water can have adverse effects on printing and thus cause the contamination of printed matter. Such a difficulty can be eliminated by adding a chelate compound to the diluting water. Preferred examples of such a chelate compound include organic phosphonic acids or phosphonoalkanetricarboxylic acids such as ethylenediaminetetraacetic acid, potassium or sodium salt thereof; diethylenetriaminepentaacetic acid, potassium or sodium salt thereof; triethylenetetraminehexaacetic acid, potassium or sodium salts thereof; hydroxyethylethylenediaminetriacetic acid, potassium or sodium

salts thereof; nitrilotriacetic acid, sodium salts thereof; 1-hydroxyethane-1,1-diphosphonic acid, potassium or sodium salts thereof; and aminotri(methylenephosphonic acid), potassium or sodium salts thereof. Besides these sodium or potassium salts of these chelating agents, organic amine salts are useful. These chelating agents are selected from the compounds which can occur stably in the surface protective agent composition and do not impair the printing properties of the printing plate. The proper amount of such a chelating agent to be added is from 0.001 to 1.0% by weight based on the weight of the surface protective agent in diluted form.

Further, an antiseptic and an anti-foaming agent may be added to the surface protective agent according to the present invention. Examples of such an antiseptic include phenol, derivatives thereof, formalin, imidazole derivatives, sodium dehydroacetate, 4-isothiazoline-3-one derivatives, benzoisothiazoline-3-one, benztriazole derivatives, amidineguanidine derivatives, quaternary ammonium salts, pyridine derivatives, quinoline derivatives, guanidine derivatives, diazine, triazole derivatives, oxazole and oxazine derivatives. The proper amount of such an antiseptic to be added is such that it can exert a stable effect on bacteria, fungi, yeast or the like. Though depending on the kind of bacteria, fungi and yeast, it is preferably from 0.01 to 4% by weight based on the weight of the surface protective agent in diluted form. Further, preferably, two or more antiseptics may be used in combination to exert an aseptic effect on various fungi and bacteria. The anti-foaming agent is preferably silicone anti-foaming agents. Among these anti-foaming agents, either an emulsion dispersion type or solubilized type anti-foaming agent may be used. The proper amount of such an anti-foaming agent to be added is from 0.001 to 1.0% by weight based on the weight of the surface protective agent in diluted form.

Besides the foregoing components, an ink receptivity agent may be added to the surface protective agent according to the present invention if desired. Examples of such an ink receptivity agent include turpentine oil, xylene, toluene, low heptane, solvent naphtha, kerosine, mineral spirit, hydrocarbons such as petroleum fraction having a boiling point of about 120 °C to about 250 °C, diester phthalates (e.g., dibutyl phthalate, diheptyl phthalate, di-n-octyl phthalate, di(2-ethylhexyl) phthalate, dinonyl phthalate, didecyl phthalate, dilauryl phthalate, butylbenzyl phthalate), aliphatic dibasic esters (e.g., dioctyl adipate, butylglycol adipate, dioctyl azelate, dibutyl sebacate, di(2-ethylhexyl) sebacate dioctyl sebacate), epoxidated triglycerides (e.g., epoxy soyabean oil), ester phosphates (e.g., tricresyl phosphate, trioctyl phosphate, trischloroethyl phosphate) and plasticizers having a solidification point of 15 °C or less and a boiling point of 300 °C or more at one atmospheric pressure such as esters of benzoates (e.g., benzyl benzoate).

Examples of other solvents which can be used in combination with these solvents include ketones (e.g., cyclohexanone), halogenated hydrocarbons (e.g., ethylene dichloride), ethylene glycol ethers (e.g., ethylene glycol monomethyl ether, ethylene glycol monophenyl ether, ethylene glycol monobutyl ether), aliphatic acids (e.g., caproic acid, enathic acid, caprylic acid, pelargonic acid, capric acid, undecylic acid, lauric acid, tridecylic acid, myristic acid, pentadecylic acid, palmitic acid, heptadecylic acid, stearic acid, nonadecanic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, heptacosanoic acid, montanic acid, melissic acid, lacceric acid, isovaleric acid) and unsaturated aliphatic acids (e.g., acrylic acid, crotonic acid, isocrtonic acid, undecyclic acid, oleic acid, elaidic acid, cetoleic acid, erucic acid, butecidic acid, sorbic acid, linoleic acid, linolenic acid, arachidonic acid, propiolic acid, stearolic acid, clupanodonic acid, tariric acid, licanic acid). Preferably, it is an aliphatic acid which is liquid at a temperature of 50 °C, more preferably has from 5 to 25 carbon atoms, most preferably has from 8 to 21 carbon atoms.

The ink receptivity agent may be used singly or in combination with one or more thereof. The ink receptivity agent is preferably used in an amount of from 0.01 to 10% by weight, more preferably from 0.05 to 5% by weight, based on the weight of the surface protective agent.

The foregoing ink receptivity agent may be contained in the oil phase in an emulsion dispersion type surface protective agent of the present invention or may be solubilized with the aid of a solubilizing agent.

The surface protective agent comprising a soybean polysaccharide according to the present invention can be easily designed as solution type, emulsion type or the like depending on the properties of the photosensitive lithographic printing plate to which it is applied. Thus, the surface protective agent according to the present invention can exert a great effect of maintaining the ink-receptivity of the image area and the water wettability of the non-image area.

The surface protective agent according to the present invention can be applied to both positive and negative lithographic printing plates. An automatic gumming machine may be used to make a uniform coating with the surface protective agent. The processing with the surface protective agent according to the present invention may be conducted immediately without rinsing after development or may be conducted after development (including rinsing, circulating rinsing with running water or wiping rinsing with a small amount of water) or processing with a rinsing solution containing a surface active agent. During printing, a satisfactorily sharp printer matter can be obtained even at the beginning of printing job without wasting

many sheets of printing paper as in the prior art.

The soybean polysaccharide used as a main component of the surface protective agent of the present invention can be used for various processing solutions for a lithographic printing plate other than the surface protective agent, such as a printing surface washing agent, an emulsion type developing ink fountain solution, a rinsing solution and a deletion fluid.

In the emulsion type plate cleaning agents according to the present invention, the acidic plate cleaning agent preferably has a pH of from 1 to 4 while the alkaline plate cleaning agent preferably has a pH of from 10 to 13.

The content of the water-soluble soybean polysaccharide in the plate cleaning agent according to the present invention is preferably from 1 to 30% by weight, more preferably from 5 to 20% by weight. The foregoing soybean polysaccharide may be used in the form of homogeneous aqueous solution in water or hot water of 50 °C or less.

The acidic emulsion type plate cleaning agent according to the present invention comprises an aqueous phase comprising (1) a water-soluble soybean polysaccharide, (2) at least one compound selected from the group consisting of phosphoric acid, polymerized phosphoric acid, alkaline metal salt thereof and organic phosphonic acid, (3) a nitrate, (4) a sulfate or bisulfate, and (5) water, and an oil phase comprising (6) a hydrocarbon solvent. The composition may further comprise (7) a surface active agent, (8) a water-soluble colloidal substance, (9) a wetting agent, (10) a thixotropic agent, and (11) a pH adjustor incorporated therein, if desired. Besides the foregoing components, additives such as a preservative, a germicide and a dye may be incorporated in the plate cleaning agent according to the present invention.

The hydrocarbon solvent as the component (6) to be incorporated in the plate cleaning agent of the present invention as an oil phase has an effect of dissolving a lithographic printing ink therein. A petroleum fraction having a melting point of from 120 to 320 °C for use in the removal of ordinary printing ink is particularly useful. The amount of the hydrocarbon solvent to be used is preferably from 5 to 60% by weight, more preferably from 10 to 40% by weight, based on the total weight of the composition. Since the component (6) is nonmiscible with water used as the component (5), the plate cleaning agent should be thoroughly stirred and dispersed before use.

The present invention will be further described in the following examples, but it should be understood that the present invention is not to be deemed to be limited thereto. All percents and parts are by weight unless otherwise indicated.

EXAMPLE 1

80 parts by weight of a water-soluble soybean polysaccharide (Soyafive-S-LN available from FUJI OIL COMPANY, LIMITED; analysis: galactose: 43.6%; arabinose: 22.5%; galacturonic acid: 2.2%; residual protein: 4.7%) and 170 parts by weight of cream dextrin (roasted dextrin) were dissolved in 728.8 parts by weight of pure water. In the aqueous solution were then dissolved 10 parts by weight of an alkyl (mainly dodecyl) diphenylether disulfonate (trade name: Sandet BL available from SANYO CHEMICAL INDUSTRIES, LTD.) as an anionic surface active agent, 3 parts by weight of di(2-ethylhexyl)sulfosuccinate (Rapizol B-80 available from NOF Corporation), 0.2 parts by weight of methyl benzoate, 1.0 part by weight of a 4-isothiazoline-3-one derivative, 3.0 parts by weight of a 85% phosphoric acid, and 5.0 parts by weight of magnesium sulfate to prepare a surface protective agent.

The surface protective agent thus obtained was then diluted with water in a proportion of 1 : 1 before use. On the other hand, a lithographic printing plate (FPS: an anodized multi-grain type positive presensitized printing plate (PS plate) available from Fuji Photo Film Co., Ltd.) was imagewise exposed to light, developed with a positive developer having the following composition in a PS automatic developing machine 900D (available from Fuji Photo Film Co., Ltd.), and then coated with the surface protective agent on the printing surface. For comparison, surface protective agents of Comparative Examples 1 and 2 as set forth in Table 1 were used to effect the similar plate making.

Developer	
Sodium silicate (SiO_2/Na_2O; molar ratio: 1.2)	2 g
Sodium ethylenediaminetetraacetate tetrahydrate	0.1 g
Water	97.9 g

Table 1

	Comparative Example 1 (g)	Comparative Example 2 (g)
Pure water	728.8	728.8
Cream dextrin	170	250
Gum arabic	80	-
Sandet BL	10	10
Rapizol B80	3	3
Methyl benzoate	0.2	0.2
4-Isothiazoline-3-one derivative	1.0	1.0
85% Phosphoric acid	3.0	3.0
Magnesium sulfate	5.0	5.0

The lithographic printing plates thus coated with the respective surface protective agent were each cut into halves, and then stored under the conditions set forth in Table 2. These lithographic printing plates were then used for printing with a Heidel SOR printing machine (available from Heidelberger Druckmaschinen Aktiengesellschaft). These lithographic printing plates were then evaluated for their properties in accordance with the evaluation method as set forth in Table 3.

The results obtained are set forth in Table 4 below.

Table 2

Mark	Storage conditions
A	Indoor Temperature: 23-26 °C/humidity: 50-70% RH; 24 hours
B	Forced storage Temperature: 45 °C/humidity: 80% RH; 24 hours

Table 3

Characteristics	Test conditions and methods
1. Ink-receptivity	Number of sheets of wasted paper from the beginning of printing job until ink can be attached to the image area to give a normal printed matter.
2. Scumming on blanket	The degree of ink adhesion on the non-image area on the blanket is visually evaluated after the printing of 1,000 sheets.
3. Scumming with fats and oils	50 μℓ of a solution of 1 g of oleic acid and 50 g of xylene is dropwise onto the non-image area to examine scumming thereon.
4. Scumming on scratched area	Scratch tester: available from Shinto Scientific Co., Ltd. The printing plate is scratched with a 0.3 R diamond stylus under a load of 20 g, 50 g, 75 g, 100 g, 150 g and 200 g. The occurrence of scumming on various scratches is examined.

Table 4

Storage conditions	Example 1		Comparative Example 1		Comparative Example 2	
	A	B	A	B	A	B
Ink-receptivity (sheets number)	10-15	15-20	40-50	300 or more	8-12	8-12
Scumming on blanket	None	None	None	None	Scumming	Scumming
Scumming with fats and oils	None	None	None	None	Scumming	Scumming
Scumming on scratched area	200 g Good	200 g Good	150 g Slight-ly poor	200 g Good	50 g Poor	50 g Poor

Table 4 shows that Example 1 is excellent in all the characteristics of surface protective agent as compared with Comparative Examples 1 and 2.

EXAMPLE 2

80 parts by weight of the same water-soluble soybean polysaccharide as used in Example 1 and 170 parts by weight of cream dextrin were dissolved in 673.8 parts by weight of pure water. In the aqueous solution thus obtained were then dissolved 5.0 parts by weight of ammonium primary phosphate, 3 parts by weight of phosphoric acid, 0.2 parts by weight of methyl benzoate and 1.0 part by weight of a 4-isothiazoline-3-one derivative to prepare an aqueous phase.

10 parts by weight of DOP (dioctyl phthalate), 5.0 parts by weight of benzyl alcohol, 25 parts by weight of a di(2-ethylhexyl)sulfosuccinate (Rapizol B-80 available from NOF Corporation) as a surface active agent, 12 parts by weight of a polyoxyethylene nonylphenol ether (Emulgen #903 available from Kao Corporation; HLB (hydrophilic-lipophilic balance): 7.8), and 3 parts by weight of sorbitan monooleate (Nonion OP-80 available from NOF Corporation) were mixed and dissolved to prepare an oil phase. The oil phase was then gradually added dropwise to the aqueous solution with stirring at 500 to 600 rpm. After the completion of dropwise addition, the mixture was subjected to homogenization by a homogenizer to obtain an emulsion type surface protective agent.

On the other hand, for comparison, surface protective agents of Comparative Examples 3 and 4 as set forth in Table 5 were prepared, and then subjected to printing test in the same manner as in Example 1. For the evaluation of emulsion stability, these specimens were observed for appearance after indoor storage (25 °C, 72 hours) and after freezing and thawing (-15 °C, 72 hours). The results are set forth in Table 6.

Table 5

	Comparative Example 3 (g)	Comparative Example 4 (g)
(Aqueous phase)		
Pure water	673.8	673.8
Cream dextrin	170	170
Gum arabic	80	-
Pinestar S*	-	80
Ammonium primary phosphate	5	5
85% phosphoric acid	3	3
Methyl benzoate	0.2	0.2
4-Isothlazoline-3-one derivative	1.0	1.0
(Oil phase)		
DOP	10.0	10.0
Benzyl alcohol	5.0	5.0
Rapizol B-80	25.0	25.0
Emulgen #903	12.0	12.0
Nonion OP-80	3.0	3.0

* Pinestar S: Modified starch for emulsion stabilization available from Matsutani Chemical Co., Ltd.

Table 6

Storage conditions	Example 2		Comparative Example 3		Comparative Example 4	
	A	B	A	B	A	B
Ink-receptivity (sheets number)	7-10	7-10	20-30	40-50	7-10	7-10
Scumming on blanket	None	None	None	None	Scumming	Scumming
Scumming with fats and oils	None	None	None	None	Some	Some
Scumming on scratched area	150-200 g None	150-200 g None	150-200 g None	150-200 g None	50 g Scumming	50 g Scumming
Emulsion stability						
Indoor	Good		Good		Fair	
After freezing and thawing	Good		Good and fair (upper phase separated)		Poor	

The above results show that the surface protective agent according to the present invention has extremely satisfactory properties as compared with the comparative examples.

As mentioned above, the present invention provides a surface protective agent having a good emulsion stability which can provide the printing plate with a good ink-receptivity and maintain the water wettability of the non-image area.

EXAMPLE 3

80 parts by weight of a water-soluble soybean polysaccharide (Soyafive-S-LN, available from FUJI OIL COMPANY, LIMITED) were dissolved in 595 parts by weight of pure water. 30 parts by weight of sodium hexametaphosphate were then dissolved in the solution with stirring. 20 parts by weight of magnesium nitrate and 5 parts by weight of sodium hydrogensulfate were sequentially added to the solution. The solution was then mixed-with 15 parts by weight of phosphoric acid (85%), 50 parts by weight of glycerin as a wetting agent, and 2.0 parts by weight of a 4-isothiazoline-3-one derivative as a preservative to prepare an

aqueous phase. On the other hand, as emulsifying agents, 20 parts by weight of Pelex OT-P (sodium dialkylsulfosuccinate available from Kao Corporation) and 10 parts by weight of Emulgen #903 (poly-(oxyethylene) nonylphenyl ether available from Kao Corporation) and 5 parts by weight of Nonion OP-80 (sorbitan monooleate available from NOF Corporation) were dissolved in 150 parts by weight of Solvent-K (hydrocarbon solvent having a melting point of from 151 to 190 °C available from Nippon Petrochemical Co., Ltd.) to prepare an oil phase.

The oil phase was gradually added dropwise to the aqueous phase with stirring at a temperature of 35 °C to prepare a dispersion which was then passed through a homogenizer to prepare an opaque emulsion type plate cleaning agent.

On the other hand, a lithographic printing plate VPS-II (anodized multi-grain type positive PS plate available from Fuji Photo Film Co., Ltd.) was imagewise exposed to light, developed with a positive developer DP-4 aqueous solution (8-fold diluted with water), rinsed, and then dried in a PS automatic developing machine 800EII (available from Fuji Photo Film, Co., Ltd.).

The foregoing printing plate was quartered, and treated under the conditions set forth in Table 7 to examine their capacity of removing scumming.

Table 7

Characteristics	Test conditions and methods
1. Scumming by air oxidation	Stored in a 150 °C drier without being coated with gum for 3 hours.
2. Scumming on scratched area	The same as in Table 3.
3. Scumming with fats and oils	The same as in Table 3.
4. Normal plate (Comparison)	Prepared under normal making conditions, coated with gum, buff-dried, and then stored.

The plates thus prepared were treated with the foregoing plate cleaning agent on a Heidelberg SOR-M type printing machine (available from Heidelberger Druckmaschinen Aktiengesellschaft) for about 30 seconds, wiped with water, and then subjected to printing. After printing began, normal printed matters showing sufficient ink affinity were first produced at the 7th to 10th sheet. No scumming occurred even after 30,000 sheets.

Halftone dots on the image area of these plates were observed. As a result, these plates showed no change in the size of halftone dot and the degree of abrasion from the normal plate D, which had not been treated with the cleaning agent. As compared with the normal plate D, which had not been treated with the cleaning agent, these plates produced printed matters having no problems such as ink scumming. The comparison between the process in which the plate treated with the plate cleaning agent is brought into contact with a water supply roller after being wiped with water and the process in which the plate treated with the plate cleaning agent is directly brought into contact with the water supply roller proved that there is little or no difference in the number of sheets required to obtain normal printed matters after the beginning of printing. In either case, normal printed matters showing sufficient ink affinity were produced at the 8th to 10th sheet.

The plate cleaning agent according to the present invention is further characterized by an extremely strong effect of inhibiting scumming caused by scratches on the hydrophilic layer on the non-image area of a lithographic printing plate as well as maintaining and enhancing the recovered hydrophilicity.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A surface protective agent for a lithographic printing plate, comprising an aqueous solution containing a film-forming water-soluble soybean polysaccharide.

2. The surface protective agent as claimed in claim 1, wherein the film-forming water-soluble soybean polysaccharide is extracted from soybean with water.

3. The surface protective agent as claimed in claim 1, wherein the film-forming water-soluble soybean polysaccharide mainly comprises galactose, arabinose and galacturonic acid.

4. The surface protective agent as claimed in claim 1, wherein the soybean polysaccharide has an average molecular weight of from 50,000 to 1,000,000 and a viscosity of from 5 to 100 cp in a 10% by weight aqueous solution at a temperature of 25 °C.

5. The surface protective agent as claimed in claim 1, wherein the content of the soybean polysaccharide is from 0.3 to 50% by weight in the surface protective agent.

6. An emulsion type plate cleaning agent comprising a film-forming polysaccharide extracted from soybean.

7. The emulsion type plate cleaning agent as claimed in claim 6, wherein the film-forming water-soluble soybean polysaccharide mainly comprises galactose, arabinose and galacturonic acid.

8. The emulsion type plate cleaning agent as claimed in claim 6, wherein the soybean polysaccharide has an average molecular weight of from 50,000 to 1,000,000 and a viscosity of from 5 to 100 cp in a 10% by weight aqueous solution at a temperature of 25 °C.

9. The emulsion type plate cleaning agent as claimed in claim 6, wherein the content of the soybean polysaccharide is from 1 to 30% by weight in the plate cleaning agent.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 11 2430

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US-A-4 347 289 (GEORGE T.COLEGROVE) * the whole document * ---	1	B41N3/08
X,P	WO-A-94 09993 (FUJI OIL CO.) * the whole document * -----	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

B41N

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	5 December 1994	RASSCHAERT, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)