United States Patent Office

3,260,198

Patented July 12, 1966

3,260,198

PROCESS FOR THE PRODUCTION OF OFFSET PRINTING PLATES

Albert Petrus Wagemans, Edegem, and Camille Angelina Vandeputte, Schoten, Belgium, assignors to Gevaert Photo-Producten N.V., Mortsel, Belgium, a Belgian company

No Drawing. Filed Apr. 24, 1964, Ser. No. 362,462
Claims priority, application Belgium, Apr. 26, 1963, 42,581, Patent 631,557
7 Claims. (Cl. 101—149.2)

This invention relates to a process for the production of offset printing plates from a material comprising a hydrophilic metal layer carrying another metal in an imagewise differentiated way, and other metal being hereinafter referred to as the image metal. The term "hydrophilic metal layer" will be understood to mean a metal layer mainly consisting of a hydrophilic metal or of a metal that can be rendered hydrophilic.

When an offset printing plate is produced from a material comprising a hydrophilic metal layer carrying an image metal that is mostly oleophilic, one may proceed in such a way that the areas of the hydrophilic metal layer free of image metal constitute the ink-repelling and thus non-printing areas.

It has now been found that an offset printing plate can be produced from a material that comprises a hydrophilic metal layer carrying an image metal, by treating this material with a solution of an organic compound that carries an oleophilic radical and that forms a compound insoluble in water with metal ions of the hydrophilic metal layer, and by subsequently uncovering the areas of the hydrophilic metal layer that are covered with image metal.

The process according to this invention thus leads to an offset printing plate possessing reversed image values with respect to that described above, as the parts of the hydrophilic metal layer that are not covered with image metal are made oleophilic as to constitute the ink-receptive and thus printing parts of the offset printing plate.

Suitable materials for use in a process according to this invention are generally known and can be produced in different ways. A bimetal layer, e.g., the bottom layer of which is hydrophilic, can be covered in the form of an image, whereupon the topmost metal layer is etched away on the non-covered areas. It is also possible to proceed according to a process described in principle in British patent specification 913,591. According to this process a light-sensitive material comprising a silver halide emulsion layer is exposed to an image and developed, whereupon the non-exposed and thus un-developed silver halide is complexed and transferred to a hydrophilic metal layer, onto which metallic silver is deposited from the complexed silver halide by the reducing action of the hydrophilic layer itself. In such a process, use can be made of a light-sensitive material that carries an unhardened surface layer on top of the silver halide emulsion layer. This is the subject matter of the French patent specification 1,381,756.

Suitable metals for the hydrophilic metal layer are mentioned in the above cited British patent specification, in the Canadian patent specification 658,050 and in the Belgian patent specification 611,026. Especially useful are highly purified aluminium and zinc that contain minute quantities of other metals such as silicon, iron and copper. The metal forming the hydrophilic metal layer may also be an alloy of hydrophilic metals or of metals adapted to be made hydrophilic and may include small amounts of impurities.

Suitable metals for the image metal are silver, copper, lead and other metals or alloys of metals which may be

slightly contaminated and which can be removed by etching without loss of the olephilic character that was conferred upon the areas not covered by image metal.

If the hydrophilic metal layer possesses sufficient mechanical strength, it is possible for the material used in the present process to consist only of such metal layer and of image metal. In many cases, however, especially when the hydrophilic metal layer is rather thin, it is preferably applied to a solid support e.g. of paper, metal or a plastic material. This application of the hydrophilic metal layer to a solid support can be performed by vacuum-metallizing so that the starting material for the present process may be produced according to the Belgian patent specification 611,026.

According to the invention, the material comprising the hydrophilic metal layer carrying an image metal is first treated with a solution of at least one organic compound that bears on oleophilic radical and is capable of forming a non water-soluble compound with metal ions of the hydrophilic metal layer. The oleophilic radical of the organic compound may arbitrarily be chosen. For instance it may be a saturated or unsaturated and occasionally branched or substituted chain with aliphatic or aromatic character.

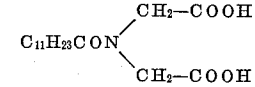
In order to be capable of forming a compound insoluble in water with metal ions of the hydrophilic metal layer e.g. with aluminium or zinc ions, the organic compound with oleophilic radical bears a functional group such as a carboxyl group, a phosphoric acid group, a phosphonic acid group and a sulphonic acid group, which can be in their salt form such as the alkali salt, the ammonium salt or the amine salt. Also organic compounds can be used that contain functions which on dissolving form such groups e.g. an hydride functions and acid chloride functions.

Organic compounds used for carrying out the first step of the present process, e.g.:

(1) Anionic wetting agents such as:

Sulphonated castor oil,

Condensation products of degraded albumin and a fatty acid chloride,



N-lauroylaminodiacetic acid

$$H_3C-(CH_2)_{15}-CH(SO_3H)-COOH$$

α-sulphostearic acid

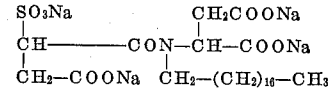
$$R-HN-CH(CH_3)-CH_2-COOH$$

N-R-β-aminobutyric acid

wherein R represents an aliphatic radical of a fatty acid which is present in cocofat in the form of its glyceride,

$$H_3C-(CH_2)_7-C(SO_3Na)=CH-(CH_2)_7-COOH$$

sodium salt of 10-sulpho-oleic acid



tetrasodium salt of N-stearyl-N-(α-sulphosuccinyl)-α-aminosuccinic acid

$$H_3C-(CH_2)_{16}-CO-N(CH_3)-CH_2-COOH$$

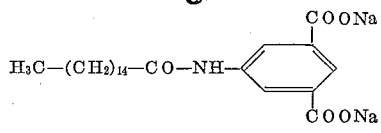
N-stearoyl-N-methylaminoacetic acid

$$H_3C-(CH_2)_{18}-CO-N(CH_3)-CH_2-COOH$$

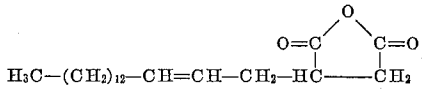
N-arachinoyl-N-methylaminoacetic acid

$$H_3C-(CH_2)_7-CH=CH-(CH_2)_7-CO-N(CH_3)-CH_2-COOH$$

N-oleoyl-N-methylaminoacetic acid



disodium salt of 5-palmitoylaminoisophthalic acid



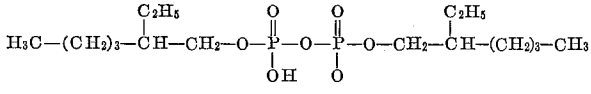
hexadecenylsuccinoic anhydride

$C_8H_{17}—O—P(OH)_2=O$

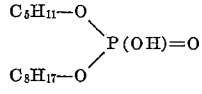
monooctyl orthophosphate

$(C_8H_{17}O)_2P(OH)=O$

dioctyl orthophosphate



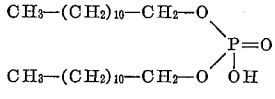
di(2-ethylhexyl) pyrophosphate



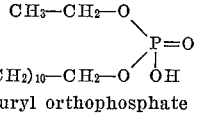
isoamyl octyl orthophosphate

$H_3C—(CH_2)_{10}—CH_2—O—P(OH)_2=O$

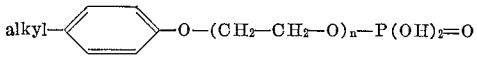
monolauryl orthophosphate



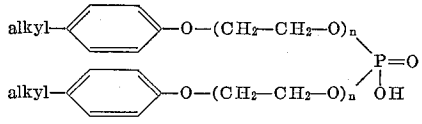
dilauryl orthophosphate



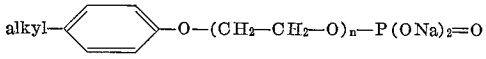
ethyl lauryl orthophosphate



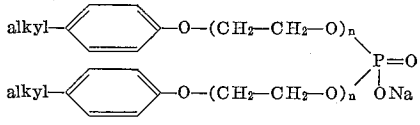
alkylphenoxypolyglycolether orthophosphate



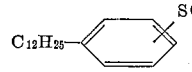
di(alkylphenoxypolyglycoether) orthophosphate



disodium alkylphenoxypolyglycolether orthophosphate



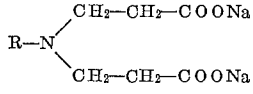
monosodium di(alkylphenoxypolyglycolether orthophosphate



sodium salt of laurylbenzenesulphonic acid

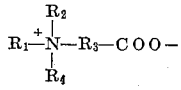
(2) Amphoteric wetting agents of the general formulae:

(a)



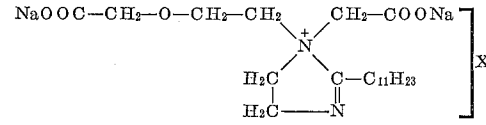
disodium N—R—β-iminodipropionate, wherein R represents an aliphatic radical of a fatty acid present in tallow in its glyceride form,

(b)



wherein R_1 represents an alkyl group having 8 to 18 carbon atoms, each of R_2 and R_4 represents a lower alkyl group which may be substituted, and R_3 represents an occasionally substituted alkylene group,

(c) N-substituted 2-R-imidazolium compounds e.g.



wherein X represents a $C_{12}H_{25}OSO_3—$ group or a hydroxyl group,

$R—NH—(CH_2)_x—COONa$

wherein R is an alkyl group having from 8 to 18 carbon atoms and x is an integer from 1 to 4.

(3) Fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid and their salts.

Most of the organic compounds mentioned hereinbefore are commercially available under different trade names. In most cases such products consist of a mixture of several organic compounds of the type intended here.

The organic compounds suitable for carrying out this first process step are dissolved in a solvent, mostly water, an alcohol, acetone or in a mixture of such solvents. In some cases the pH of a solvent has to be changed in order to enable the latter to dissolve certain organic compounds. For example, the above-mentioned non-substituted fatty acids are not soluble in common water, but are in water the pH of which is increased above 8.5 by means of sodium hydroxide or another alkali.

The treatment of a material comprising a hydrophilic metal layer and an image metal with a solution of an organic compound can be performed by rubbing this material with a plug of wadding soaked with this solution.

The duration of the treatment depends on different factors such as the kind of the organic compound, its concentration in the solution, the temperature, the pH of the solution, etc.

Mostly the treatment is carried out at room temperature. While the concentration of the organic compound may vary within wide limits, it is preferably, however, between 0.1 and 25% by weight per part by volume of the solution. Under these circumstances, the duration of the treatment lies between 5 seconds and 2 minutes.

The quality of an offset printing plate obtained according to this invention is improved with increasing adherence of the compound insoluble in water to the areas of the hydrophilic metal layer that are not covered by image metal. It appears that the adherence is improved by the presence of some compounds such as thickening agents in the solution for the first treatment. Suitable thickening agents are e.g. glycerin, carboxymethylcellulose, soluble alginates, poly(vinyl methacrylate) poly(acrylic acid), poly(methacrylic acid), etc. They start to be effective when added to the solution in a concentration of from 0.5 to 5% by weight per part by volume.

It has been found too that, according to this invention, a higher quality offset printing plate can be obtained if the surplus organic compound with the oleophilic radical is removed at least partially, e.g., by rinsing the material with water or by wiping it with a dry tissue, before uncovering the areas of the hydrophilic metal layer that are covered by image metal.

The step of uncovering the hydrophilic metal layer on the areas that are covered by image metal can be performed by treating the material with an aqueous solution of an oxidizing agent for this metal. This treatment can also take place by rubbing. In most cases it takes from a few seconds up to some minutes. Suitable oxidizing agents that do not attack the oleophilic character of the areas that are not covered by image metal are e.g. potassium hexacyanoferrate (III), potassium permanganate, potassium dichromate, potassium peroxodisulphate, the mix-

ture of potassium iodide with iodine, and the iron (III) salt of ethylenediaminetetraacetic acid.

These oxidizing agents are dissolved in concentrations varying between 0.2 and 20% by weight per part by volume of the solution. To these solutions may be added thickening agents too, such as those mentioned above, in approximately analogous concentrations. It appears that these thickeners protect against aerial oxidation those areas of the hydrophilic metal layer that lie under the image metal and are ultimately uncovered. Moreover, the hydrophilic properties of the said areas are enhanced by said thickeners.

In some cases the oxidation products of the image metal are soluble in the oxidizing solution alone. If not, the oxidation products must be eliminated in some other way. This can be done, e.g., by adding to this bleaching solution compounds that enable the solution to dissolve such products, or by treating the image metal subsequently to the oxidative treatment with a solvent for these products, or with a liquid containing ingredients that make possible the dissolution of the oxidation of the oxidation products in this liquid. If the image metal contains e.g. silver, an aqueous solution of sodium thiosulphate, potassium thiosulphate, ammonium thiosulphate, potassium metabisulphite, ammonium thiocyanate or thiourea is especially suited to dissolve any oxidation products of silver that are insoluble in the oxidation liquid. Such an auxiliary treatent for the elimination of the oxidation products of the image metal can also take place in the presence of thickeners such as the above-mentioned ones, which are then preferably incorporated into the used processing liquid in the indicated concentrations.

Occasionally the solution used for the elimination of those oxidation products which are insoluble in the bleaching solution can also be utilized for the elimination of the excess of organic compound bearing an oleophilic radical, since it appears that the supplementary elimination of the insoluble oxidation products of the image metal is promoted thereby and because the solution is readily available.

An offset printing plate prepared according to the invention can, of course, be given all kinds of additional treatments such as rinsing and an after-treatment with an etching solution that improves the hydrophilic properties of the non-printing areas. Such an etching solution has been described in the British patent specification 913,591. The essential constituents of such an etching solution may be incorporated into the bleaching solution or into a processing solution which is used afterwards. The strength of the offset printing plate and especially of its hydrophobic areas can still be improved by rubbing the printing plate before its processing with a hydrophobic protective lacquer such as described in the French patent specification 1,290,784 or by subjecting it to a customary lithographic treatment such as inking and by subsequently heating it in order to cause the ink to adhere to the printing areas.

An offset printing plate obtained according to the present invention is of excellent quality both with respect to its aptitude for producing very sharp prints as well as with respect to its durability.

The following examples illustrate the invention.

Example 1

A silver image is transferred according to the method described in Example 1 of the Japanese Patent No. 313,605 (or its corresponding British Patent 946,538 and Canadian Patent 658,050) to a brushed aluminium foil consisting of 99.5% of aluminium and 0.5% of magnesium and silicon.

After the formation of this image the material is vigorously rubbed with a plug of wadding soaked with a solution of the following composition:

Water, ccs.	50
Ethanol, ccs.	50
Sodium stearate, g.	1

The surplus sodium stearate is then removed with a dry plug of wadding.

Subsequently the material is treated for approximately 1 min. with a bleaching solution of the following composition:

Water, ccs.	100
Potassium hexacyanoferrate (III), g.	10
Potassium bromide, g.	1

Finally the material is treated with a 10% aqueous solution of sodium thiosulphate, which dissolves the oxidation product of the image metal. An offset printing plate is obtained, the printing areas of which are constituted by the areas not covered by image metal.

Example 2

An aluminium foil carrying a silver image as described in Example 1 is vigorously rubbed with a plug of wadding soaked with a solution of the following composition:

Water, ccs.	10
Glycerin, ccs.	80
Ethyl lauryl orthophosphate, g.	0.75

The surplus ethyl lauryl orthophosphate is removed with the aid of a solution of the following composition:

Water, ccs.	50
Glycerin, ccs.	50
Anhydrous sodium thiosulphate, g.	5

The image metal is oxidized by treating the material with a solution of the following composition:

Water, ccs.	50
Glycerin, ccs.	50
Potassium hexacyanoferrate (III), g.	5
Potassium bromide, g.	0.5

Subsequently the oxidized image metal is dissolved by means of a plug of wadding soaked with the solution utilized for eliminating the surplus ethyl lauryl orthophosphate.

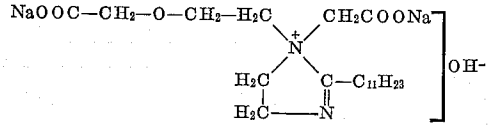
An offset printing plate is obtained in which the areas not covered with image metal constitute the printing areas.

For improving the hydrophilic properties the resultant offset printing plate is rubbed in with a lithographic preparation as described in Example 1 of the Canadian patent specification 658,050. Subsequently, the offset printing plate is rubbed with a hydrophobic lacquer as described in the French patent specification 1,290,784 in order to consolidate the printing areas.

Example 3

A zinc foil bearing silver as image metal is treated for 30 sec. with a plug of wadding soaked with a solution of the following composition:

Water, ccs.	25
1% aqueous sodium alginate solution, ccs.	200
Compound of the formula, g.	1



The surplus product with the hydrophilic radical is removed by treating the material with the following solution:

Water, ccs.	50
1% aqueous solution of sodium alginate, ccs.	50
Potassium metabisulphite ($K_2S_2O_5$), g.	5

Subsequently the material is rubbed in with a bleaching solution of the following composition:

Water, ccs.	50
1% aqueous solution of sodium alginate, ccs.	50
Potassium permanganate, g.	0.5

Finally, the finished offset printing plate is obtained by treating the material with the above-mentioned solution of potassium metabisulphite once again. The areas which were not covered with silver constitute the printing areas.

Example 4

A zinc foil bearing silver as image metal is successively:

(1) Rubbed in with a solution of the following composition:

Water, ccs.	25
2% aqueous solution of carboxymethylcellulose, ccs.	200
Monosodium salt of 10-sulphooleic acid, g.	0.5

(2) Rinsed with water,

(3) Rubbed in with a solution of the following composition:

Water, ccs.	50
2% aqueous solution of carboxymethylcellulose, ccs.	50
Potassium iodide, g.	5
Iodine, g.	1

(4) Rubbed in with a solution of the following composition:

Water, ccs.	50
2% aqueous solution of carboxymethylcellulose, ccs.	50
Anhydrous sodium sulphite, g.	0.5
Anhydrous ammonium thiosulphate, g.	5

The quality of the offset printing plate thus obtained can be improved even further by rubbing it with a lithographic preparation and finally with a hydrophobic lacquer as described in the French patent specification 1,290,784.

Example 5

An aluminium foil bearing a silver image as described in Example 1 is rubbed in with a solution of the following composition:

Water, ccs.	25
5% aqueous solution of poly(acrylic acid), ccs.	200
Laurylbenzene sodium sulphonate, g.	3

The surplus laurylbenzene sodium sulphonate is removed by rubbing the material with a sponge soaked with a solution of the following composition:

Water, ccs.	50
5% aqueous solution of poly(acrylic acid), ccs.	50
Anhydrous potassium thiosulphate, g.	8

For bleaching away the image metal, the material is treated with a solution of the following composition:

Water, ccs.	50
5% aqueous solution of poly(acrylic acid), ccs.	50
Potassium dichromate, g.	5
Potassium bromide, g.	1

For eliminating the oxidation products of the image metal, the material is treated once again with the solution which was utilized before in order to remove the surplus of organic compound with the oleophilic radical.

An offset printing plate of excellent quality is obtained. The areas which were not covered with image metal are hydrophilic and consequently non-printing.

Example 6

An aluminium foil bearing a silver image as described in Example 1 is rubbed in with a solution of the following composition:

Water, ccs.	25
Glycerin, ccs.	200
Sodium myristate, g.	0.5

The surplus solution is removed from the foil with a dry tissue. Subsequently the silver image is eliminated with a solution of the following composition:

Water, ccs.	50
2% aqueous solution of sodium alginate, ccs.	50
Potassium peroxodisulphate ($K_2S_2O_8$), g.	2.5

The resulting offset printing plate is of excellent quality.

Example 7

A silver image is transferred according to the silver complex diffusion transfer process to a brushed aluminium foil consisting of 99.5% of aluminium and 0.5 of magnesium and silicon. In this process a light-sensitive material is utilized which bears on the light-sensitive layer a covering layer substantially consisting of hydroxyethyl starch (degree of molar substitution: ±0.27). This material is the subject matter of the French patent specification 1,381,756.

This aluminium foil carrying a silver image is then rubbed in with a solution of the following composition:

Water, ccs.	25
2% aqueous solution of carboxymethylcellulose, ccs.	200
N-stearyl-N-methylaminoacetic acid, g.	0.25
N-arachidoyl-N-methylaminoacetic acid, g.	0.25

The surplus solution is removed from the foil with a dry tissue.

The silver image is eliminated with a solution of the following composition:

Water, ccs.	50
2% aqueous solution of carboxymethylcellulose, ccs.	50
Sodium iron (III) salt of ethylenediamine tetraacetic acid, g.	2
Sodium salt of ethylenediamine tetraacetic acid, g.	0.5
Anhydrous ammonium thiosulphate, g.	5
Ammonium thiocyanate, g.	0.1
Anhydrous sodium sulphite, g.	2

The printing properties of the resultant offset printing plate can be improved even further by consolidating the printing areas as described in Example 2.

Example 8

An aluminium foil bearing a silver image as described in Example 7 is rubbed in with a solution of the following composition:

Ethanol, ccs.	25
Glycerin, ccs.	200
Stearic acid, g.	0.5

The surplus stearic acid is eliminated with a tissue soaked with a solution of the following composition:

Water, ccs.	50
1% aqueous sodium alginate solution, ccs.	50
Anhydrous sodium thiosulphate, g.	5

The aluminium present under the silver image is uncovered again by treating the foil with a solution of the following composition:

Water, ccs.	50
1% aqueous solution of sodium alginate, ccs.	50
Potassium bromide, g.	0.5
Potassium hexacyanoferrate (III), g.	5

Finally, the oxidation products of the silver image are

removed by treating the foil with the above-mentioned solution of sodium thiosulphate once again.

An offset printing plate of excellent quality is obtained.

We claim:

1. A process for reversing the printing and non-printing areas of an off-set printing plate comprising a hydrophilic layer consisting essentially of at least one metal of the group consisting of aluminum and zinc and a layer of silver metal superimposed on selected areas of said hydrophilic layer corresponding to an image, which process comprises the steps of:

(1) Treating said plate with an organic compound adapted to ionize in solution to form a group reactive with ions of the metal of said hydrophilic layer to produce in situ at the surface of said hydrophilic layer a water-insoluble compound repelling water from said layer surface, said reactive group containing oleophilic and acid hydrophilic moieties and reacting through the latter, said organic compound being applied to said plate in solution in a solvent permitting ionization thereof, and

(2) Thereafter, removing the silver image layer by treating said plate with an oxidizing agent for silver and dissolving the resultant oxidation products in a solvent therefor.

2. The process of claim 1 wherein said organic compound is a member of the group consisting of anionic and amphoteric surface active agents.

3. The process of claim 1 wherein at least a portion of any surplus amount of said organic compound is removed from said plate prior to removal of the image metal layer therefrom.

4. The process of claim 1 wherein at least one of said steps of treating the printing plate and removing the image metal layer is carried out in the presence of a thickening agent.

5. The process of claim 1 wherein the resultant off-set printing plate with the reversed printing and non-printing areas is treated with a solution containing constituents adapted to improve the hydrophilic properties of the exposed hydrophilic metal surfaces.

6. The process of claim 1 wherein the resultant off-set printing plate with the reversed printing and non-printing areas is treated with a solution containing constituents adapted to strengthen the printing areas thereof.

7. The process of claim 1 wherein said silver image layer is obtained by reduction of dissolved silver salts diffused onto the surface of said hydrophilic metal layer from an imagewise exposed photographic emulsion arranged in contact with said surface in the presence of a silver halide solubilizing agent.

References Cited by the Examiner

UNITED STATES PATENTS

19,626	3/1858	Cutting et al.	101—149.2
1,742,710	1/1930	Krebs	96—29 X
2,297,929	10/1942	Wise	101—149.2
3,161,508	12/1964	Hepher et al.	96—29

ROBERT E. PULFREY, *Primary Examiner.*

DAVID KLEIN, *Examiner.*

JANYCE A. BELL, *Assistant Examiner.*