United States Patent Office 3,016,823 Patented Jan. 16, 1962

3,016,823
LITHOGRAPHIC PRINTING PLATE AND METHOD OF MAKING THE SAME

John F. Thurlow, Gorham, Maine, assignor to Fitchburg Paper Company, Fitchburg, Mass., a corporation of Massachusetts

No Drawing. Filed June 11, 1958, Ser. No. 741,222
17 Claims. (Cl. 101—149.2)

This invention relates to lithographic printing plates and the method of making the same.

Conventional lithographic printing plates such as are used in producing relatively small editions usually comprise a paper base which has been treated to impart strength and render it dimensionally stable, and such a base is then overlayed with several coats of a suitable composition having lithographic properties, i.e., capable of developing ink-receptive, water-repellant areas constituting the printing surfaces, and water-receptive, ink-repellant areas constituting the non-printing surfaces. Other plates now or heretofore commercially available were either a metal foil such as copper, zinc or aluminum, laminated to a suitable lacking, or a parchmentized paper laminated to a suitable backing.

The efficacy and life of all such plates depends primarily on the ability to maintain the printing and non-printing areas, and in order to assure a commercially satisfactory plate it is often necessary to apply several coatings, including prime and barrier coats in order to prevent migration of any oleophilic constituents of the base into the lithographic surface. When such plates embody in their planographic surface materials such as casein or gelatin or polyvinyl alcohol, a tendency to curl may develop which requires still further treatment, such as coating of the back side, in order to reduce curl and other complications impairing usefulness. A further disadvantage in the manufacture of many of the presently-available commercial plates which are made on a paper base is that, inasmuch as coatings are applied from an essential aqueous medium, the surface of the base stock may become disturbed (roughened or dimpled) during the coating operation and, in consequence, it may be necessary to calender after each coating operation—with the resulting extra waste and cost.

The principal objects of the present invention are to provide a relatively inexpensive lithographic printing plate which overcomes the aforementioned objectionable features and to provide an efficient and reliable method of making the same. Further objects will be apparent from a consideration of the following disclosure and specific examples illustrative of what is now considered the preferred procedures.

In accordance with the present invention I provide a lithographc plate which comprises a base impregnated (throughout) and/or carrying at least on one surface a coating consisting essentially of from 10 to 60 parts, by weight, of an olephilic agent (preferably an adhesive film former) and from 40 to 90 parts, by weight, of a hydrophilic agent or water-receptive material (such as a water-receptive pigment or adhesive or wetting agent or a combination of these), the oleophilic agent and hydrophilic agent both being soluble or dispersible in a common essentially non-aqueous, organic solvent.

The base may comprise any suitable material, preferably a relatively flexible sheet material of adequate strength to withstand use on an offset press and capable of receiving and retaining a coating or impregnation of the lithographic composition. Economic considerations indicate the use of paper, preferably a coated or heavily-filled paper the weight of which may vary from 1.3 to 5.0 ounces per square yard. Where a paper, coated or otherwise, is sufficiently impregnated, with a composition such as described above, there is no tendency to curl. Since the composition is essentially non-aqueous in nature there is so little disturbance of the surface that subsequent mechanical flattening, as by calendering, is not necessary.

The oleophilic agent may comprise any of the well-known synthetic polymers such as the vinyls, e.g., polyvinyl acetate, polyvinyl chloride, vinyl acetate, vinyl chloride copolymer, polystyrene, the alkyds, the polyesters, the phenolics, the polyamides, the acrylics, chlorinated hydrocarbons, cellulose esters such as the nitrate and acetate, propionate, butyrate, etc., certain cellulose ethers such as ethyl cellulose, the silicone resins, the epoxy resins, certain hydrocarbon resins such as the cumarone indene, polyterpene resins, etc., provided they satisfy the compatibility requirements of being soluble or dispersible in a volatile, essentially non-aqueous, organic solvent along with a selected water-receptive component or components.

The hydrophilic agent or water-receptive material, if of the wetting type is preferably non-ionic which has been found to give superior results. Where a pigment is required a fine-particle silica (SiO_2) or silica gel has been found to have superior water-receptivity, although clays, insoluble carbonates and other pigments have been found suitable particularly when used in combination with water-receptive adhesives such as starches and gums or in combination with soluble non-ionic water-receptive materials of the wetting-agent type. Combinations of silica and clays or insoluble carbonates have been found superior to clays or carbonates used alone.

The ratio of oleophilic agent to hydrophilic agent will vary in accordance with the particular components selected; the coated base stock and the solvents used for applying the oleophilic and hydrophilic agents will also be a major factor in the choice of the exact ratio to be used for the production of a successful planographic surface but in general the ratio will fall within the above-specified limits.

The essentially non-aqueous organic solvent may be a single organic solvent or a solvent mixture and this term, as herein used, is intended to connote either so long as the aqueous content does not exceed 30% by weight. Apart from the solvency requirements, the solvent preferably should be non-toxic, relatively inexpensive and have a boiling point between 30° and 365° C. at atmospheric pressure. Typical examples of such solvents are xylene, toluene, cyclohexanone, petroleum ether, ethyl alcohol, methyl alcohol, acetone, methyl ethyl ketone, methyl isobutyl ketone, dioxane, glacial acetic acid, ethylene dichloride, methyl cellosolve, etc.

Whenever possible the coating or impregnating composition is preferably in the form of an organosol in which the water-receptive material has been dissolved or uniformly dispersed; and where penetration of the base or sheet material is necessary or desirable a less concentrated organosol or solution is used in order to insure adequate penetration. The lithographic composition may be applied by any of the conventional coating and/or impregnating machines capable of producing a smooth essentially continuous film at least on one face of the carrier sheet or base. The term "continuous film" as herein used connotes a film or coating or surface containing, evenly distributed throughout its mass, molecules, particles or areas having either hydrophilic or oleophilic character, the latter preferably providing a lesser surface area than the former (and thus does not necessarily imply an unbroken film formed from a continuity of the same chemical compound or species) so that the image from a typical lithographic marking instrument will be received and retained but, in those areas not thus imaged, the slightly greater areas of water-receptive centers will exert

a dominant effect and will thus assure a water-wettable, clean, non-imaged area when run on an offset press.

It can thus be seen that if the areas of hydrophilicity are insufficient in number or are of insufficient strength the plate thus made will not run clean. On the other hand, if the areas of hydrophilicity are too numerous or too large or are composed of a material having too-great a hydrophilic character the image may be weak or may easily wash off after a few copies; moreover, unless the components are carefully selected and the proper balance maintained the resulting surface (as in the case of an excessively water-receptive surface) will not receive, let alone retain, an image from a pen, pencil, typewriter or other marking instrument. The coated sheets may be cut for use directly on the cylinder roll of an offset press or it may be laminated to a carrier sheet which is applied to the cylinder roll.

Specific examples illustrative of the foregoing are as follows:

EXAMPLE 1

Equal parts of a silicone resin (SR–82) and a non-ionic wetting agent (nonyl-phenol-polyethylene glycol-ether, sold under the trade designation Neutronyx 675) were separately dissolved in toluene to produce solutions of between 15% and 20% solids and the two solutions mixed to provide a saturating solution. A coated book paper (2.6 oz. per sq. yard) was run through the saturating solution in conventional manner and excess solution was removed by passage through squeeze rolls. The saturated and coated paper thus produced was then dried at a rate which prevented blistering or the development of surface defects. The dried paper (which now weighed 2.8 oz. per sq. yard) was then cut up into plates stored for a short period, and then were run on an offset press in customary manner. Such plates produced 400–600 satisfactory reproductions or editions before their lithographic properties were appreciably impaired.

Further tests showed that the ratio of the particular oleophilic component (SR–82) to water-receptive material or wetting agent could be varied from 30:70 to 55:45 without a perceptible difference in the resulting lithographic properties. The apparent greater amount of oleophilic agent present in the solution when a 55:45 ratio was used did not, of course, maintain after drying inasmuch as the native hydrophilicity of the original coating caused the hydrophilic character to predominate after treatment.

Further tests on several other coated printing papers made by various manufacturers demonstrated that satisfactory plates, insofar as the planographic properties were concerned, could be made in all cases although, since the coatings were markedly different in nature, different papers sometimes required different ratios of the two components and some of these coated papers showed superior coating strengths or other desirable properties essential for successful plates.

Since some of these coated papers had coating which had nearly the correct balance for good planographic properties further tests were made in an attempt to run untreated sheets; and such tests demonstrated that untreated coated paper would run only a few copies before disintegrating in most cases because neither the coatings, nor the papers were sufficiently water-resistant.

Further tests showed that the concentrations could be varied between 5 and 25% solids and, in some cases, the ratio of oleophilic to water-receptive or hydrophilic agent could be as low as 20:80 without appreciably sacrificing results, and that omission of either the oleophilic or the water-receptive agent produced inferior results.

EXAMPLES 2–5

In the following examples the procedure described in Example 1 was repeated, using the same oleophilic agent, but with different types of polyethyleneoxide-polyoxypropylene wetting agents, (sold under the trade designation Pluronic) as indicated in the following table:

Table I

Example No.	Film Former or Oleophilic Agent	Hydrophilic or Wetting Agent	Concentration of Solution, Percent	Weight of Paper (Air-Dry Basis) oz./sq. yd.		No. of Satisfactory Copies
				Untreated	Treated	
2	SR-82	Pluronic F-38	10	2.6	2.7	400
3	SR-82	Pluronic F-68	10	2.6	2.7	300
4	SR-82	Pluronic F-77	15	2.6	2.8	400
5	SR-82	Pluronic F-88	20	2.6	2.9	200

Further tests with these water-receptive agents and that of Example 1 revealed that, depending somewhat on the weight of the paper and its coating, the combined weight of the two agents retained on and in the paper and its coating could be varied between 0.1 and 1.0 ozs. per square yard without appreciably sacrificing satisfactory results.

Further tests with the formulae shown in Table I and with the formulae discussed in Example 1 showed that uncoated, wet-strength papers could be treated to produce printing plates but, in the absence of the pigmented surface present on coated paper, relatively few successful copies could be run on the usual offset press. With such wet-strength papers the image was often poorly retained by the plate and was usually not satisfactorily reproduced on the copy. When such paper contained considerable mineral filler or a surface wash of adhesive and pigment (such as applied by the usual size press) much better results were obtained. When non-wet-strength uncoated papers were treated the surfaces of the resulting plates rapidly disintegrated under the stresses of press operations.

EXAMPLES 6–18

The procedure set forth in Example 1 was repeated with various oleophilic agents, using a ratio of oleophilic agent to hydrophilic agent of 20:80 and a concentration of 10% of the active ingredients. In all examples shown in the following table the water-receptive agent was Neutronyx 675.

Table II

Example No.	Film Former or Oleophilic Agent	Number of Satisfactory Copies
6	Duraplex C-45LV (linseed oil modified alkyd resin)	200
7	Duraplex A-29 (soy bean oil modified alkyd resin)	200
8	Chlorowax 70 (high melting chlorinated paraffin)	300
9	Acryloid B-72 (acrylic ester resin)	200
10	Piccolyte S-135 (terpene resin)	100
11	Piccolyte S-115-L (terpene resin)	100
12	Cumar P-25 (cumarone indene resin)	100
13	Cumar MH-2 (cumarone indene resin)	100
14	Cumar W-2 (cumarone indene resin)	100
15	Duraplex ND-77B (coconut oil modified alkyd resin)	100
16	Amberlac 292-G (castor oil modified alkyd resin)	100
17	Duraplex C-55X (castor oil modified alkyd resin)	100
18	Pliolite VT (vinyl toluene/butadiene resin)	50

In each of the foregoing examples the paper base carried 0.2 to 0.4 ounce of active ingredients per square yard of air-dried stock.

Further experiments with the oleophilic agents of Tabel II showed that the ratio of oleophilic agent to hydrophilic agent could be as low as 10:90 without sacrificing satisfactory results.

Further experiments showed that numerous other oleophilic agents could be substituted for those of Table II to produce equally satisfactory results providing, of course, that solvents other than toluene were used in

order to assure complete solubility or dispersibility of the active ingredients. Oleophilic agents thus tested were several phenolic resins (such as Schenectady 6600 and 8010 which were dissolved in methyl cellosolve and acetone) and epoxy resins (such as Araldite 502 and 6071 which were dissolved in ethyl acetate), as well as other commercially available solvent soluble hydrocarbon resins (such as Neville 570–525 and Neville R–1) of a complex chemical nature.

EXAMPLES 19–31

The procedures set forth in Examples 1–18 were repeated with numerous additional hydrophilic agents of the surface active wetting agent type used in combination with SR–82 (the oleophilic agent) according to the conditions shown in Table III to produce a weight of the active ingredients between .2 and .6 oz. per sq. yd. of coated paper which, prior to treatment, had a total weight of 2.6 oz. per sq. yd. Concentrations of the impregnating solutions ranged between 5 and 20% active ingredients but, in the majority of cases, were 10%; the ratio of oleophilic to hydrophilic agent was 40/60 in all cases.

Table III

Example No.	Hydrophilic or Wetting Agent	Solvent
19	Polyalkylene glycol ether (Tergitol XD)	Toluene.
20	Alkylphenyl ether of polyethylene glycol (Tergitol NP-40).	Do.
21	Polyoxyethylene sorbitan tristearate (Tween 65)	Do.
22	Polyoxyethylene monostearate (Tween 61)	Do.
23	Polyoxyethylene propylene glycol monostearate	Do.
24	Polyoxyethylene stearate	Do.
25	Polyethylene glycol ester of rosin (AR100)	Do..
26	Carbowax 1000 monostearate	Acetone.
27	Carbowax 4000 monostearate	Do.
28	Ethylene glycol monostearate	Toluene.
29	Polyethylene glycol 400 monostearate	Acetone.
30	Polyethylene glycol 400 distearate	Do.
31	Polyethylene glycol 600 distearate	Do.

Further experiments shown that Acryloid B–72 and other of the previously-used oleophilic agents could be substituted for the SR–82 in examples 19–31 without appreciably sacrificing satisfactory results although, when B–72 was used, plates sometimes performed better when the ratio of oleophilic agent to wetting agent was 20:80 instead of 40:60.

Additional experiments showed that numerous other solvents such as ethyl or methyl alcohol, dioxane, ethyl acetate, butyl acetate, ethylene dichloride, cyclohexanone etc. could be used in place of all or part of the acetone or toluene used in the foregoing experiments without materially affecting results.

Plates made in Examples 19–31 and the further experiments above described, produce as many as 500 satisfactory copies when run on the usual offset press. Poorest results were generally obtained with those hydrophilic agents having the greatest effect on surface tension inasmuch as the coated surface and the paper itself were more susceptible to deterioration during press operation thus demonstrating that while a water-receptive or hydrophilic agent is essential for this invention, with powerful wetting agents (i.e. those most markedly lowering the surface tension) great care in the selection and amount used must be exercised if the plate is to run more than a few copies; similarly, with the more powerful agents, great care must be exercised in the manufacture of the coated or uncoated base stock if the plate is to run more than a few copies.

EXAMPLES 32–35

The procedures set forth in the previous examples were repeated using 10% solutions in either acetone or toluene or both of a 40:60 ratio oleophilic agent: water-receptive agent, care being taken to use water-receptive agents of low surface activity. The oleophilic agents used were either SR–82 or Acryloid B–72. The weights of active ingredients retained in coated paper of original weight 2.6 oz. per sq. yd. were between .2 and .6 ozs. per sq. yd. The materials thus tested are listed in Table IV.

Table IV

Example No.:	Water-Receptive or Hydrophilic Agent
32	[1] Carbowax 750
33	[1] Carbowax 1000
34	[1] Carbowax 4000
35	[1] Carbowax 6000

[1] High molecular weight polyethylene glycols.

Plates in these examples gave excellent copy although the plates of Examples 32 and 33 were somewhat superior. Plates in these examples showed greatly improved resistance to disintegration during press operations.

Further experiments in repetition of these and earlier examples demonstrated that excellent plates could be made on heavier coated papers weighing up to 5.0 ozs. per sq. yd. and that in general the heavier the coating the more superior the plate in terms of its performance on the offset press. Plates made from these heavier coated papers were found to carry as much as 1.0 oz. of the active ingredients per sq. yd.

EXAMPLE 36

In all of the preceding examples the solution or suspension was applied to a previously-coated sheet of printing paper the coating of which was composed essentially of a suitable binder (such as a starch, casein, gelatine or alpha protein) and an insoluble mineral filler (such as clay, calcium carbonate or barium sulfate, etc.). The heavier weights of retained ingredients sometimes gave to the treated sheets a waxy and therefore hard-to-mark surface.

In the present example the formulae of Examples 1–35 were found to give greatly improved results, which is to say that the plates were easier to mark upon and the plates and copy remained cleaner, if between 2 and 20% by weight of the active ingredients were replaced by a fine particle-size water-receptive pigment, preferably a silica or silica gel (such as Syloid 978 or Syloid 244). This pigment, having the ability to remain for a time in suspension in the essentially non-aqueous organic solvents used in this invention, also greatly improved the performance of plates made from uncoated wet-strength paper and thus, it is apparent, was bound to some degree to the surface of either coated or uncoated papers.

EXAMPLE 37

A superior plate, in terms of ease of marking and general press performance, was made by applying (prior to treatment with any of the formulae of Examples 1–36) to a wet-strength sheet an aqueous coating which, in its dry state, was composed essentially of 100 parts of fine-particle-size silica or silica gel and between 40 and 100 parts of starch or casein. The weight of the dried silica-starch or silica-casein coating amounted to 0.1 to 1.2 oz. per sq. yd. before treatment with solvent solutions of oleophilic: hydrophilic agents of the type described in Examples 1–35. Plates thus made gave exceptionally sharp images and clean non-image areas.

Further experiments showed that essentially the same results could be obtained if only a portion of the usual clay or carbonate or other pigments (as used in the coating of the papers serving as base-stocks for the plates of Examples 1–35) were replaced by silica or silica gel; the replaceable portion comprised 25 or more parts per 100 of the pigment.

EXAMPLES 38 TO 45

Other formulations showing both high and low power wetting agents and different solvents and solvent mixtures are set forth in the following table:

Table V

Example No.	Oleophylic Agent	Hydrophilic Agent	Solvent or Solvent Mixture
38	SR-82	Neutronyx-675	Toluene.
39	SP-6600	do	Acetone-Methyl Cellosolve.
40	SP-8010	do	Do.
41	Araldite 6071	do	Acetone.
42	SR-82	Carbowax 1000 Monostearate.	Toluene.
43	SR-82	Carbowax 4000 Monostearate.	Do.
44	SR-82	Methoxy Polyethylene Glycol.	Do.
45	SP-6600	do	Acetone-Methyl Cellosolve.

In each of the foregoing examples the ratio of oleophilic to hydrophilic agent was 20:80 and the treating solution had a combined solids content of oleophilic and hydrophilic of 10% and in addition carried 10% of finely divided silica. Exceptionally satisfactory plates were produced when the treating composition was applied to a paper base as in Example 37.

I claim:

1. A lithographic printing plate comprising a base having on one surface a coating consisting essentially of a homogeneous mixture of from 10 to 60 parts by weight of an oleophilic, water-insoluble film former and from 40 to 90 parts, by weight, of a hydrophilic non-ionic wetting agent, the hydrophilic agent being soluble in an organic solvent in which said film former is soluble, said wetting agent and film former each being evenly distributed throughout the mass of said coating without being reacted together and imparting their hydrophilic and oleophilic characteristics to said coating effectively for lithographic printing.

2. A lithographic printing plate comprising a fibrous sheet impregnated with and carrying at least on one face a coating consisting essentially of a homogeneous mixture of from 10 to 60 parts by weight of an oleophilic, water-insoluble film former and from 40 to 90 parts, by weight, of a hydrophilic non-ionic wetting agent, the hydrophilic agent being soluble in an organic solvent in which said film former is soluble, said wetting agent and film former each being evenly distributed throughout the mass of said coating without being reacted together and imparting their hydrophilic and oleophilic characteristics to said coating effectively for lithographic printing.

3. A lithographic printing plate comprising a sheet of paper having on one surface a coating consisting essentially of a homogeneous mixture of from 10 to 60 parts by weight of an oleophilic, water-insoluble film former and from 40 to 90 parts, by weight, of a hydrophilic non-ionic wetting agent, the hydrophilic agent being soluble in an organic solvent in which said film former is soluble, said wetting agent and film former each being evenly distributed throughout the mass of said coating without being reacted together and imparting their hydrophilic and oleophilic characteristics to said coating effectively for lithographic printing.

4. A lithographic printing plate comprising a sheet of coated paper impregnated with and carrying at least on one surface a coating consisting essentially of a homogeneous mixture of from 10 to 60 parts by weight of an oleophilic, water-insoluble film former and from 40 to 90 parts, by weight, of a hydrophilic non-ionic wetting agent, the hydrophilic agent being soluble in an organic solvent in which said film former is soluble, said wetting agent and film former each being evenly distributed throughout the mass of said coating without being reacted together and imparting their hydrophilic and oleophilic characteristics to said coating effectively for lithographic printing.

5. A lithographic printing plate as set forth in claim 1, wherein said coating includes a uniform dispersion of finely divided silica in an amount not exceeding the weight of the other ingredients of said coating.

6. A lithographic printing plate as set forth in claim 1, wherein said wetting agent is a nonyl-phenol-polyethylene glycolether.

7. A lithographic printing plate comprising a base having on one surface a coating consisting essentially of a homogeneous mixture of from 10 to 60 parts by weight of a silicone resin and from 40 to 90 parts, by weight, of a hydrophilic non-ionic wetting agent, the wetting agent being soluble in an organic solvent in which the silicone resin is soluble, said silicone resin and wetting agent imparting oleophilic and hydrophilic characteristics to said coating effective for lithographic printing.

8. A lithographic printing plate as set forth in claim 7, wherein said coating includes a uniform dispersion of finely divided silica in an amount not exceeding the weight of the other ingredients of said coating.

9. A lithographic printing plate comprising a base having on one surface a coating consisting essentially of from 10 to 60 parts by weight of a soluble phenol-aldehyde resin and from 40 to 90 parts, by weight of a hydrophilic non-ionic wetting agent, the wetting agent being soluble in an organic solvent in which the resin is soluble, said resin and wetting agent imparting oleophilic and hydrophilic characteristics to said coating effective for lithographic printing.

10. A lithographic printing plate as set forth in claim 9, wherein said coating includes a uniform dispersion of finely divided silica in an amount not exceeding the weight of the other ingredients of said coating.

11. A lithographic printing plate comprising a base having on one surface a coating consisting essentially of from 10 to 60 parts by weight of an epoxy resin and from 40 to 90 parts, by weight of a hydrophilic non-ionic wetting agent, the wetting agent being soluble in an organic solvent in which the resin is soluble, said resin and wetting agent imparting oleophilic and hydrophilic characteristics to said coating effective for lithographic printing.

12. A lithographic printing plate as set forth in claim 11, wherein said coating includes a uniform dispersion of finely divided silica in an amount not exceeding the weight of the other ingredients of said coating.

13. A lithographic printing plate comprising a base having on one surface a coating consisting essentially of from 10 to 60 parts by weight of a hydrocarbon resin and from 40 to 90 parts, by weight of a hydrophilic non-ionic wetting agent, the wetting agent being soluble in an organic solvent in which the resin is soluble, said resin and wetting agent imparting oleophilic and hydrophilic characteristics to said coating effective for lithographic printing.

14. A lithographic printing plate as set forth in claim 13, wherein said coating includes a uniform dispersion of finely divided silica in an amount not exceeding the weight of the other ingredients of said coating.

15. A lithographic printing plate as set forth in claim 1, wherein said wetting agent is essentially a polyethylene oxide-polyoxypropylene wetting agent.

16. A lithographic printing plate as set forth in claim 15, wherein the coating includes approximatey 10% by weight of finely divided silica.

17. The method of preparing a lithographic printing plate which comprises applying to one surface of a base a volatile organic solvent solution of a coating composition consisting essentially of a homogeneous mixture of from 10 to 60 parts by weight of an oleophilic, water-insoluble film former and from 40 to 90 parts, by weight, of a non-

ionic wetting agent, the wetting agent and the film former both being in solution in said solvent, and removing said solvent to provide a coating having lithographic properties, said wetting agent and film former each being evenly distributed throughout the mass of said coating without being reacted together and imparting their oleophilic and hydrophilic characteristics to said coating effectively for lithographic printing.

References Cited in the file of this patent

UNITED STATES PATENTS

2,280,986	Toland et al.	Apr. 28, 1942
2,692,826	Neugebauer et al.	Oct. 26, 1954
2,724,665	Oransky et al.	Nov. 22, 1955
2,778,301	Brinnick et al.	Jan. 22, 1957
2,865,873	Hodgins et al.	Dec. 23, 1958