

UNITED STATES PATENT OFFICE

2,597,865

FINISHING VARNISH FOR APPLICATION
OVER LITHOGRAPHIC INKPaul W. Greubel, Great Neck, N. Y., assignor to
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corporation of New JerseyNo Drawing. Application April 8, 1948,
Serial No. 19,876

22 Claims. (Cl. 260—33.2)

1

The present invention relates generally to finishing varnishes for lithographic inks and more particularly to novel improvements in those finishing varnishes which are applied over wet lithographic inks printed upon various web or sheet materials especially sheet metal, such as tin plate,terne plate, enameled sheet metal, etc. and to methods of varnishing over wet lithographic ink, in which the methods the ink pigment is flocculated upon application of the varnish, thereby preventing bleeding and ridging of the ink.

For many years it has been the practice, for example, in the decorated or lithographed sheet metal container art, to pass freshly lithographed metal sheets thru ovens for the purpose of drying the lithographic ink printed thereon before applying the finishing varnish which constitutes the final coating operation. Finishing varnishes are used to protect the lithographed surface and to improve its appearance by producing a hard, protective and glossy finish.

Later, attempts were made to economize these operations by applying the wet finishing varnish directly over the wet ink and then passing the web or sheet thus coated thru the drying oven, thus drying both the wet ink and the wet varnish coats in a single operation. This process is known in the art as wet varnishing or wet ink varnishing. It saves considerable time and labor and would have many advantages if it were completely successful. However, the results obtained are unpredictable and have been far from satisfactorily uniform. It has been partially successful with only a relatively few finishing varnish formulations. In addition to restricting the use of many desirable and commercially required varnish formulations, the main difficulty has been inferior appearance such as lack of sharpness and lack of gloss in the finished lithographed product. More specifically, the inferior appearance is due to the bleeding or running of the ink under the leveling action of the varnish coating, the ink flowing away from the printed areas at the edges; also the ink flows into macroscopic ridges or waves in the more solid areas thereby producing a mottled and/or raised effect.

After extensive observations, experiments and tests conducted over a considerable period of time, I discovered the causes or reasons for those undesirable results. I found that they are due to certain physico-chemical phenomena similar to those which occur in the process of detergency. By experimenting with a great many different varnishes and inks, applying each varnish over a

2

given ink and conversely applying a given varnish over each of a series of different inks and also mixing the respective inks and varnishes and observing them microscopically I found that in all cases of failures there occurred a local movement of the ink film similar in action to that of detergency or washing away and that the pigment particles of the ink film were always deflocculated. Close examination revealed that the two undesirable phenomena, i. e. bleeding or running and ridging or waving are the same in principle, each being the result of a disturbance or movement of the ink as leveling of the finishing varnish occurs. I also found that in all cases where bleeding and ridging did not occur, the pigment was always flocculated and where these undesirable phenomena did occur the pigment was always in a state of deflocculation.

Upon discovering the reason or cause of the trouble, i. e. deflocculation of the ink pigment, I started the search for a proper remedy. It occurred to me that the difficulties could probably be overcome by searching out and utilizing lithographic inks and finishing varnishes which are completely or at least substantially immiscible. I soon discovered that this approach to the solution of the problem was impractical in view of the present state of the art. The film forming materials used in both inks and varnishes are usually essentially of the same general nature, i. e. both may be made from drying oils with or without resins or the finishing varnish usually contains a solvent which is also a solvent for the ink vehicle. Therefore, this method of approach would be successful only with very few and very carefully selected materials. This would severely limit the choice of materials from which the inks and finishing varnishes could be made. Since commercial requirements make it imperative to have as wide a range of materials available as possible for use in this process, I searched for other means of solving the problem.

Next I thought of producing a flocculated ink by incorporating a flocculating agent in the ink during its manufacture. This method also proved impractical because an ink strongly flocculated before printing possesses certain undesirable characteristics which make it difficult to handle in the printing presses.

I then discovered that all the desirable results from a commercial use standpoint can be best secured by the incorporation of a flocculating agent or a combination of flocculants in a finishing varnish which on contact with the wet lithographic ink positively induces a strongly

flocculated structure in the ink pigment and prevents bleeding or ridging of the ink when the varnish is applied over the wet ink.

Water and certain water soluble organic substances are known to induce flocculation in systems of solids in organic vehicles. Starting with this general knowledge I experimented with a great number of likely materials to test their suitability for my specific purpose. I discovered that while such flocculating materials come from various chemical classes or groups the suitable and successful ones, irrespective of their varying chemical composition, ultimately group themselves under a common class which can be defined by their common physical characteristics. They must all be liquids. They must all be substantially immiscible or at least of a very low order of miscibility with the ink vehicle-finishing varnish system. The term "immiscible" is used in a relative sense. They must all have certain polar behavior.

Polar compounds are those in which the force uniting the atoms in the chemical bond is the electrostatic attraction between oppositely charged particles. This electrostatic attraction is present in ionizable compounds and in compounds having electrostatic dissymmetry or oppositely charged groups in their spatial structure.

Immiscible liquids are those wherein one liquid will not blend or dissolve in another or will blend or dissolve only to a very limited degree, such that when they are poured together two distinct or separate layers or phases result. Absolute immiscibility may be said to be non-existent and may be assumed to be useless as a flocculant since this would imply absolute immiscibility with the other liquids in the wet varnish system. "Immiscible" in connection with the present invention refers to a relatively low order of miscibility in the ink vehicle-finishing varnish system. The force of flocculation induced by immiscible liquids decreases as miscibility increases.

And finally these materials must be incorporated in the finishing varnish in certain percentages by weight, which vary with different varnish compositions and ink compositions, which percentages will be effective in inducing immediate flocculation of the pigment in the lithographic ink.

While immiscibility or substantial immiscibility of the flocculating liquids is a necessary characteristic I discovered that because of the low order of miscibility of these compounds this desirable characteristic is accompanied by the phenomenon of sometimes establishing a two-phase system in the finishing varnish. Therefore it is sometimes necessary that the immiscible flocculant be rendered sufficiently accessible to the lithographic pigment so that it can come into intimate contact with said pigment whereby it increases the interfacial tension between the pigment surface and ink vehicle, which will result in immediate, strong flocculation of the lithographic ink pigment. I solved this problem by introducing a coupling agent or mutual solvent into the varnish composition. The coupling agent or mutual solvent must be miscible with the ink vehicle, the varnish vehicle and the flocculant. The function of the coupling agent or mutual solvent is to maintain the varnish-flocculant mixture in a single continuous phase before application of the varnish to the inked surface and further to continue to maintain a single liquid phase when such mixture is applied to the wet

ink so that the flocculant can readily penetrate the ink vehicle in order to gain access to the ink pigment. Where a certain solvent already in the varnish composition is capable of functioning as a coupling agent, no additional or a lesser amount of coupling agent is required.

Among the flocculants which I have found to be satisfactory are:

- (1) Water
- (2) Alkanols of from one to three carbon atoms inclusive such as methanol, ethanol, isopropanol, normal propanol
- (3) Lactic acid (commercial U. S. F. grade)
- (4) Formamide
- (5) Dihydric alcohols of from two to four carbon atoms inclusive, such as: Ethylene glycol, propylene glycol, trimethylene glycol, diethylene glycol, etc.
- (6) Glycerol

For the purpose of the present invention I prefer to emphasize ethylene glycol.

All of the flocculants which I found to be satisfactory including those specifically mentioned come under the definition "relatively oil immiscible, water soluble polar liquids." The word "oil" in this definition, for the purpose of my invention, means the water insoluble oil, resin or other film forming materials constituting the vehicle of lithographic inks. My extensive experiments and tests conclusively show that no material or compound which does not come under this definition functions as a satisfactory flocculant and conversely all materials or compounds which do answer this definition are good flocculants. Ethylene glycol falls under the classification of relatively oil immiscible water soluble polar liquids.

Ethylene glycol, with or without coupling agents, is incorporated into the finishing varnish formulation, in such percentages by weight of complete finishing varnish as will result in the required or optimum flocculation in the wet ink film.

The percentage of flocculant required varies in accordance with the particular varnish composition in which it is to be embodied. It varies in accordance with the flocculating force or ability of the particular flocculant itself. And it may vary in accordance with the particular lithographic ink pigment which it is to flocculate. For example, I have found that Milori blue requires a higher percentage of flocculant than any other lithographic ink pigment, and that when bleeding and ridging of this pigment is stopped, bleeding and ridging of all other pigments also is controlled.

The required percentage of flocculant in each commercial formulation of finishing varnish for stopping either bleeding or ridging can be readily determined by the following methods:

Bleeding

The method consists of preparing several aliquots of a given varnish, keeping one aliquot free of flocculating agent as a control, and adding progressively increasing amounts of flocculating agent or mixture of flocculants, and coupling agent when necessary, to the remainder. A particular ink is rolled onto a strip of white enameled metal plate, leaving a sharp, white uninked margin. One strip of wet-inked plate is dipped (white margin down) into each varnish-flocculating agent mixture, and then allowed to drain. Bleeding, if present, will readily

be observed against the background of the white enamel.

Ridging

To determine whether ridging is overcome, the preparation of finishing varnish-flocculating agent aliquots, and rolling of a particular ink on a strip of white enameled metal plate is identical with the procedure described under bleeding. However, instead of dipping the strip of wet-linked metal plate into the varnish, the varnish is applied over the wet ink by means of a roller. The plate remains flat at all times during this procedure. Ridging, if it occurs, can best be observed by looking at the ink from a 90 degree angle.

I have found that ethylene glycol is very effective in percentages of from about 2 to 14 per cent, but the practical range (which may be considered the critical range) is wider and extends from about 1.0 per cent to 17 per cent, depending upon the varying factors heretofore mentioned.

Where a coupling agent or mutual solvent is required, I found that the most satisfactory compounds are those which have a group that is water-like in character or which may be said to impart water soluble characteristics. The most desirable coupling agents all have a free organic hydroxyl or alcohol group or an acetylated alcohol group and all come under the classifications of aliphatic alcohols and glycol monoethers or acetates of the glycol monoethers. They may be graphically represented by $R(O)R'$ in which R is a straight chain aliphatic carbon chain of four (4) to eight (8) carbon atoms or a glycol monoether in which both the glycol and ether portions of the molecule have from two (2) to four (4) carbon atoms, and R' is a hydrogen atom or an acetate radical.

The following are suitable as coupling agents either singly or in combination for all my purposes:

Butyl alcohol (butanol)
Hexyl alcohol (hexanol)
Octyl alcohol (octanol)
Ethylene glycol monobutyl ether (butyl Cello-solve)
Ethylene glycol monoethyl ether (Cellosolve)
Diethylene glycol monobutyl ether (butyl Carbitol)
Acetic ester of diethylene glycol monobutyl ether (butyl Carbitol acetate)

The film forming materials from which metal decorating finishing varnishes are generally prepared and with which the principles of the present invention may be successfully employed include:

A. Polyester polymers

ALKYD RESINS

Alkyd resins formed by the reaction of polyhydric alcohols and polybasic carboxylic acids and their anhydrides, modified with non-drying, semi-drying or drying oils, with or without rosin, with or without mono or poly-functional phenolic bodies.

71.0% Soya modified alkyd resin solution 50% solids (film former)
5.7% Ethylene glycol (flocculant)
23.3% Diethylene glycol monobutyl ether (coupling agent)

2

58.8% Phenol modified alkyd resin solution 50% solids (film former)

9.4% Ethylene glycol (flocculant)
31.8% Diethylene glycol monobutyl ether (coupling agent)

B. Polyethers of polyhydroxy compounds

ALLYL ETHERS OF POLYHYDROXY COMPOUNDS

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34.7% Allyl starch (solid) (film former)
30. % Toluene (resin solvent)
13.8% Ethylene glycol (flocculant)
21.3% Diethylene glycol monobutyl ether (coupling agent)

C. Condensation polymers of aldehydes and amines or alcohols

15 ALKYLATED REACTION PRODUCTS OF AMINES, SUCH AS UREA OR MELAMINE AND AN ALDEHYDE, SUCH AS FORMALDEHYDE

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79.2% Urea-melamine-aldehyde resin solution 50% solids (film former)
2.4% Catalyst
6.3% Ethylene glycol (flocculant)
8.6% Diethylene glycol monobutyl ether (coupling agent)
1.0% Spermaceti wax (lubricant)
2.5% Xylene (solvent for lubricant)

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33.3% Urea melamine aldehyde resin solution 50% solids (film former)
10.0% Ethylene glycol (flocculant)
6.7% Diethylene glycol monobutyl ether (coupling agent)

35 Condensation polymer of a polyvinyl alcohol and aldehyde

POLYVINYL-BUTYRAL

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6.5% polyvinyl butyral (solid) (film former)
41.6% Butanol (resin solvent)
7.4% Ethylene glycol (flocculant)
44.5% Ethylene glycol monobutyl ether (coupling agent)

D. Vinyl halide-vinyl ester copolymers

VINYL CHLORIDE-VINYL ACETATE

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16.0% Vinyl chloride-vinyl acetate copolymer (solid) (film former)
28.0% Methyl isobutyl ketone
24.0% Xylene
12.0% Isophorone
6.4% Ethylene glycol (flocculant)
13.6% Diethylene glycol monobutyl ether (coupling agent)

E. Rosin modified oleoresinous varnish

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77.4% Rosin modified oleoresinous varnish solution 70% solids (film former)
3.1% Ethylene glycol (flocculant)
19.5% Diethylene glycol monobutyl ether (coupling agent)

The formulae cited are typical examples of my invention. Many more could be added.

A lubricant may be added to the finishing varnish if the sheet metal is to be subjected to fabricating processes after lithographing. The addition of a lubricant (which is optional) will, of course, vary the indicated percentages of ingredients to a slight degree. Customarily, the lubricant is added in the form of a solution and

the amount is regulated so that the lubricant solids are equivalent to approximately 2 to 4 per cent of the resin solids in the finishing varnish.

The inclusion or exclusion of a lubricating material has been found to be without effect on the pigment flocculating ability of the ethylene glycol.

The finishing varnish may be prepared without regard to whether the entire film former is manufactured in a single operation, or if a "hard" resin is first formed and then combined with a drying oil in a varnish kettle or if a solid resin is dissolved in solvents. Further, these groups of film formers may be used singly, or in any compatible combination, depending on the film characteristics desired. Anyone skilled in the art of varnish making will be able to prepare the various varnishes which may be used in connection with my disclosed invention.

The above examples are for the purpose of illustrating the essential spirit of the present invention, that is to say, the finishing varnish is formulated in such a manner as to enable the same to induce a flocculated structure in the lithographic ink.

My extensive experiments conclusively indicate that the finishing varnishes covered by the invention hereinbefore described may be applied over any and all wet lithographic inks composed of organic and/or inorganic pigments dispersed in a drying oil and/or resin modified drying oil and/or other ink vehicles such as are ordinarily used in lithography, especially metal lithography.

It is thought that the invention and many of its attendant advantages will be understood from the foregoing description, and it will be apparent that various changes or modifications may be made in the compositions described without departing from the spirit and scope of the invention or sacrificing all of its material advantages, the compositions hereinbefore described being merely a preferred embodiment thereof.

I claim:

1. A finishing varnish for application over wet lithographic ink, said finishing varnish consisting of an organic solvent soluble resinous condensation product of an amine and an aldehyde as a film forming ingredient, and a volatile organic solvent mixture for said ingredient, said mixture being miscible with the ink vehicle and containing from 1 to 17% by weight based on the finished varnish of ethylene glycol as an ink pigment flocculating agent and sufficient coupling agent selected from the group consisting of unsubstituted monohydric alkanols having from 4 to 8 carbon atoms and glycol monoethers having from 2 to 4 carbon atoms in the glycol portion of the molecule and having one free hydroxyl group and the other hydroxyl group etherified with an aliphatic hydrocarbon substituent having from 2 to 4 carbon atoms to maintain the ingredients in a single liquid phase.

2. A finishing varnish for application over wet lithographic ink, said finishing varnish consisting of an organic solvent soluble synthetic resin selected from the group consisting of alkyd resins, resinous polyethers of polyhydroxy compounds, condensation polymers of amines and aldehydes, condensation polymers of aldehydes and polyvinyl alcohol, and copolymers of vinyl halides and organic acid vinyl esters, as film forming ingredients, and a volatile organic solvent mixture for said ingredients, said mixture being miscible with the ink vehicle and containing from 1 to 17% by weight based on the finished varnish

of ethylene glycol as an ink pigment flocculating agent and sufficient unsubstituted monohydric alkanol having from 4 to 8 carbon atoms to maintain the ingredients in a single liquid phase.

3. A finishing varnish for application over wet lithographic ink, said finishing varnish consisting of an organic solvent soluble synthetic resin selected from the group consisting of alkyd resins, resinous polyethers of polyhydroxy compounds, condensation polymers of amines and aldehydes, condensation polymers of aldehydes and polyvinyl alcohol, and copolymers of vinyl halides and organic acid vinyl esters, as film forming ingredients, and a volatile organic solvent mixture for said ingredients, said mixture being miscible with the ink vehicle and containing from 1 to 17% by weight based on the finished varnish of ethylene glycol as a pigment flocculating agent and sufficient glycol monoether having from 2 to 4 carbon atoms in the glycol portion of the molecule and having one free hydroxyl group and the other hydroxyl group etherified with an aliphatic hydrocarbon substituent having from 2 to 4 carbon atoms to maintain the ingredients in a single liquid phase.

4. A finishing varnish for application over wet lithographic ink, said finishing varnish consisting of an organic solvent soluble synthetic resin selected from the group consisting of alkyd resins, resinous polyethers of polyhydroxy compounds, condensation polymers of amines and aldehydes, condensation polymers of aldehydes and polyvinyl alcohol and copolymers of vinyl halides and organic acid vinyl esters as film forming ingredients, and a volatile organic solvent mixture for said ingredients, said mixture being miscible with the ink vehicle and containing from 1 to 17% by weight based on the finished varnish of ethylene glycol as an ink pigment flocculating agent, and sufficient coupling agent selected from the group consisting of unsubstituted monohydric alkanols having from 4 to 8 carbon atoms and glycol monoethers having from 2 to 4 carbon atoms in the glycol portion of the molecule and having one free hydroxyl group and the other hydroxyl group etherified with an aliphatic hydrocarbon substituent having from 2 to 4 carbon atoms to maintain the ingredients in a single liquid phase.

5. A method of varnishing over wet lithographic ink, comprising, printing a pigmented lithographic ink on a sheet of web material and flocculating the ink pigment by applying over the wet ink a finishing varnish that is substantially miscible with the ink vehicle and which contains an organic solvent soluble film forming resin in solution in a volatile organic solvent, sufficient oil immiscible-water soluble pigment flocculating agent selected from the group consisting of unsubstituted monohydric alkanols having from 1 to 3 carbon atoms and glycols having from 2 to 4 carbon atoms to effect rapid ink pigment flocculation, and sufficient coupling agent selected from the class consisting of unsubstituted monoalkanols having from 4 to 8 carbon atoms and glycol monoethers in which the glycol portion of the molecule has from 2 to 4 carbon atoms and one free hydroxyl group and the other hydroxyl group etherified with an aliphatic hydrocarbon substituent having from 2 to 4 carbon atoms, to maintain the ingredients in a single liquid phase.

6. The method of claim 5 in which the resin is a synthetic resin.

7. The method of claim 6 in which the resin is

formed by polymerization of a compound containing a vinyl group.

8. The method of claim 6 in which the resin is selected from the group consisting of alkyd resins, resinous polyethers of polyhydroxy compounds, condensation polymers of amines and aldehydes, condensation polymers of aldehydes and polyvinyl alcohol, and copolymers of vinyl halides and organic acid vinyl esters.

9. The method of claim 8 in which the resin is an alkyd resin.

10. The method of claim 8 in which the resin is a condensate of an amine and an aldehyde.

11. The method of claim 8 in which the resin is a resinous polyether of a polyhydroxy compound.

12. The method of claim 7 in which the resin is a copolymer of a vinyl halide and vinyl acetate.

13. The method of claim 5 in which the web material is a metal sheet.

14. The method of claim 13 in which the metal sheet is tin plate.

15. The method of claim 13 in which the metal sheet is steel.

16. The method of claim 5 in which the flocculating agent is ethylene glycol in concentrations of 1 to 17% by weight of the finished varnish.

17. The method of claim 5 in which the coupling agent is an unsubstituted monohydric alkanol having from 4 to 8 carbon atoms.

18. The method of claim 5 in which the coupling agent is a glycol monoether having from 2 to 4 carbon atoms in the glycol portion of the molecule and having one free hydroxyl group and the other hydroxyl group etherified with an aliphatic hydrocarbon substituent having from 2 to 4 carbon atoms.

19. A finishing varnish for application over wet lithographic ink, said finishing varnish consisting of an alkyd resin as a film forming ingredient and a volatile organic solvent mixture for said resin, said mixture being miscible with the ink vehicle and containing from 1 to 17% by weight based on the finished varnish of ethylene glycol as an ink pigment flocculating agent and sufficient coupling agent selected from the group consisting of unsubstituted monoalkanols having from 4 to 8 carbon atoms and glycol monoethers in which the glycol portion of the molecule has from 2 to 4 carbon atoms and one free hydroxyl group and the other hydroxyl group etherified with an aliphatic hydrocarbon substituent having from 2 to 4 carbon atoms, to maintain the ingredients in a single liquid phase.

20. A finishing varnish for application over wet lithographic ink, said finishing varnish consisting of an organic solvent soluble resinous polyether of a polyhydroxy compound as a film forming ingredient, and a volatile organic solvent mixture for said ingredient, said mixture being miscible with the ink vehicle and containing from 1 to 17% by weight based on the finished varnish of ethylene glycol as an ink pigment

flocculating agent and sufficient coupling agent selected from the class consisting of unsubstituted monoalkanols having from 4 to 8 carbon atoms and glycol monoethers in which the glycol portion of the molecule has from 2 to 4 carbon atoms and one free hydroxyl group and the other hydroxyl group etherified with an aliphatic hydrocarbon substituent having from 2 to 4 carbon atoms, to maintain the ingredients in a single liquid phase.

21. A finishing varnish for application over wet lithographic ink, said varnish consisting of an organic solvent soluble resinous copolymer of a vinyl halide and an organic acid vinyl ester as a film forming ingredient and a volatile organic solvent mixture for said ingredient, said mixture being miscible with the ink vehicle and containing from 1 to 17% by weight based on the finished varnish of ethylene glycol as an ink pigment flocculating agent and sufficient coupling agent selected from the group consisting of unsubstituted monoalkanols having from 4 to 8 carbon atoms and glycol monoethers in which the glycol portion of the molecule has from 2 to 4 carbon atoms and one free hydroxyl group and the other hydroxyl group etherified with an aliphatic hydrocarbon substituent having from 2 to 4 carbon atoms, to maintain the ingredients in a single liquid phase.

22. A finishing varnish for application over wet lithographic ink, said varnish consisting of an organic solvent soluble alkyd resin admixed with a drying oil as a film forming ingredient and a volatile organic solvent mixture for said ingredient, said mixture being miscible with the ink vehicle and containing from 1 to 17% by weight based on the finished varnish of ethylene glycol as an ink pigment flocculating agent and sufficient coupling agent selected from the group consisting of unsubstituted monoalkanols having from 4 to 8 carbon atoms and glycol monoethers in which the glycol portion of the molecule has from 2 to 4 carbon atoms and one free hydroxyl group and the other hydroxyl group etherified with an aliphatic hydrocarbon substituent having from 2 to 4 carbon atoms, to maintain the ingredients in a single liquid phase.

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