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3,054,751

MAGNETIC LITHOGRAPHIC INKS

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No Drawing. Filed Dec. 30, 1958, Ser. No. 783,997
5 Claims. (Cl. 252—62.5)

This invention relates to magnetic lithographic inks and more particularly to oleophilic lithographic inks containing hydrophilic magnetic pigments.

Lithographic printing is well known in the art and generally involves the use of a plate having a portion of its surface treated so as to be wetted by a solution which is essentially water, and having the remainder of its surface treated to resist wetting by the solution and to be wetted by an oleophilic ink. The solution is applied to the plate by such applicators as, for example, rollers carrying a film of the solution. The plate subsequently contacts an ink laden roller. Ink on the roller is repelled by the water-bearing areas of the plate and accepted by non-water bearing areas thereof. The ink image is subsequently transferred to a work surface which prints the image on a desired sub-strate, such as, for example, a sheet of paper. Many compositions of suitable inks and fountain solutions are well known in the lithographic printing arts and have been employed for many years.

With recent developments of automation in accounting there have been developed devices for identifying characters printed with magnetic inks and, in certain applications, it is highly desirable to employ the lithographic printing process for depositing these inks.

Magnetic inks employ magnetic pigments in powder form. It is essential that a high pigment loading is provided in the ink in order that suitable signal strength will be obtained when the printed characters are sensed by magnetic sensing means. These high pigment loadings of magnetic pigments increase the emulsification tendencies of the ink. This increase results, in substantial part, from the hydrophilicity of magnetic pigment particles. Thus there tends to form, on the ink applying roller of the lithographic press, an emulsification of water picked up from the water wet surface of the plate. This emulsion adversely effects the printing operation, producing a deposition of magnetic ink particles on the water wet plate and a deposition of water particles on the ink receiving areas of the plate. Not only does this produce bad printing and spotty work but also the magnetic characteristics of the printed areas are lowered, adversely affecting subsequent magnet sensing operation.

It is the primary object of this invention to provide a lithographic ink containing a magnetic pigment treated to present hydrophobic surfaces for reducing emulsification tendencies of the ink.

More specifically, it is among the objects of the invention to reduce emulsification tendencies of the lithographic ink containing a magnetic pigment in order to provide better magnetic properties of characters printed thereby, better drying of the printed ink due to minimization of the water content thereof, darker and better appearance of the printed ink due to the minimization of water content thereof, a wider latitude in press control, i.e. in the control of the application of the fountain solution and the ink, thus simplifying press control and the capacity for long run operation with fountain solutions previously not usable.

A further object of the invention is to provide better wetting of the pigment particles by the varnishes which

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are contained in lithographic inks to provide better rheological properties of the ink, better printing coverage by the ink, and darker or deeper appearance of the printed ink.

A further object of the invention is to provide wider latitude in the use of fountain solutions. Such latitude is particularly desirable when paper masters or plates are employed. Paper masters are specifically treated and require the use of special fountain solutions which may adversely affect inks and have greater tendencies than other fountain solutions to emulsify with inks.

A further object of the invention is to provide a lithographic ink employing magnetic pigments of desirable magnetic properties wherein undesirable coloration properties of the pigment are overcome simultaneously with a reduction in hydrophilicity of the magnetic pigment particles.

These and other objects of the invention are accomplished primarily by a lithographic ink containing magnetic pigments in which the pigment particles are treated to present hydrophobic surfaces.

Hereafter the term "magnetic pigments" will be employed to refer to any of numerous well known magnetic pigments suitable for use in magnetic inks. Such pigments include, for example: gamma ferric oxide with remanences of 1,500 gaussess or more, coercivities of between 200 and 400 oersteds, and particle size range of 1-10 microns; natural or artificial magnetites of similar properties; uniaxial iron of similar properties; small particle magnetic alloys; and cobalt, nickel and barium ferrites and similar materials.

One general form of treatment which may be employed for reducing the emulsification tendencies of magnetic pigments, such as those listed above, is to coat the pigment particles with a suitable resin. Such resins may, for example, include: silicones, vinyl acetates, chlorides, polyethylenes, polyamides, phenolics, alkyds, coumarone-indene, and epoxy resins.

One method of accomplishing resin coating of pigment particles is by providing the resin in fluid form, such as in a molten state, and stirring the pigment into the resin. Thereafter the resin is cooled and crushed, and the pigment particles are then recovered in coated form. Another fluid coating method involves the use of heated two roller mill dispersion of a pigment in a resin, followed by cooling and chip crushing.

Another method which may be employed for coating the pigment particles with a resin involves the deposition of the resin from a solution onto the pigment particles. This may be done, for example, by fractionation or by pigment seeding techniques. In pigment seeding, pigment particles are added to a supersaturated solution of a resin in a solvent while the resin is precipitated by cooling or by digestion. Precipitated resin will accumulate on the pigment particles and coat each of the particles. In fractionation processes the resin is dissolved in a solvent, pigment is then stirred into the solution and while stirring a poor solvent is added to the solution—throwing the resin out of solution. The resin coming out of solution coats the pigment particles thinly and evenly.

Following are examples of resins and solvents which may be employed in seeding techniques.

	Resin	Solvent
1	melamine resins	xytol/butanol.
2	cyclized rubber	trichlorethylene, xytol or toluol.
3	silicones	xytol.

Following are examples of resins and solvents which may be employed in fractionation techniques.

	Resin	Good Solvent	Poor Solvent
1.-----	vinyl chloride.-----	tetra hydrofuran-----	benzene.-----
2.-----	chlorinated paraffin.-----	nitrobenzene.-----	methyl alcohol.-----
3.-----	zein.-----	ethanol.-----	water.-----

In the foregoing precipitation coating methods the amount of resin precipitated should be equal to the oil absorption of the pigment, i.e., the amount of resin precipitated should be sufficient to cover all of the powder surface.

Following is an example of an ink formulation embodying pigment particles treated by the general form of treatment described above:

70 gms. artificial magnetite, cubical particles averaging 5 microns in size, coated with 10% silicon resin.
9 gms. 100% solid isophthalic alkyd varnish, viscosity: Z 2½ Gardner tube at 77° F.
8 gms. solvent-resin varnish, consisting of 50 parts by weight modified phenol formaldehyde resin in petroleum solvent with boiling point in 500-600° F. range.
4 gms. paraffin oil, light, viscosity 125/135.
2 gms. 21% cobalt drier.
7 gms. black colorant, consisting of 20 parts impingement carbon black, particle size 24 milli-microns, flushed into #0 and #3 linseed oils.

A second general form of treatment which may be employed for reducing the emulsification tendencies of pigments, such as those listed above, is to coat the pigments with dye surfactants by laking procedures.

Well known laking procedures involve the use of dyestuffs in the form of molecular chains having one end portions of hydrophilic nature and the other end portion of oleophilic nature. Various well known dyestuffs may be employed and upon application to magnetic pigment particles, attach to the particle by their hydrophilic portion leaving their oleophilic portion extending outwardly from the pigment particles and presenting hydrophobic surfaces to any water particles which may be encountered.

Following are examples of laking procedures which may be employed:

Example 1

The following materials are mixed to form a slurry:

Water (hot)-----	Gms. 30,000
Acetic acid, 56%-----	100
Rhodamine 6 GDN-----	500
Heat to 90° C.; stir until dissolved. Add:	
Densad carbonyl iron oxide regular-----	1,055

The following materials are mixed to form a solution:

Water (hot)-----	Gms. 6,000
Sodium tungstate, cryst.-----	995
Sodium molybdate, cryst.-----	95
Di-sodium phosphate-----	115
20° Baumé muriatic acid-----	800

The solution is added to the slurry forming an insoluble complexed dye including rhodamine tungstate; which attaches itself to the surfaces of the oxide particles, coating them as described above.

A further advantage obtained through these laking processes in the treatment of magnetic pigments for use in lithographic inks is that magnetic pigments of highly desirable magnetic properties may be employed even though these pigments are of undesirable coloration.

Following is an example of an ink formulation embodying pigment particles treated by the second form of treatment described above:

55 gms. ferric oxide, gamma crystalline form, obtained by oxidation of pure iron globules created by decomposition of carbonyl iron, said globules to be under 10 microns in diameter. Resulting ferric oxide is densad, to lower oil absorption, then laked with rhodamine tungstate-molybdate (described above).

5 gms. red colorant, as red lake 7013.

16 gms. 100% solids isophthalic alkyd varnish, viscosity Z 2½ Gardner tube at 77° F.

10 15 gms. varnish, consisting of 50 parts rosin modified phenol formaldehyde resin, melting point 127-133° C. in petroleum solvent, boiling point 590° F. Viscosity: Z 6¾ at 77° F. Gardner tube.

4 gms. petroleum solvent, boiling point 535° F.

15 2 gms. 21% cobalt drier.

3 gms. proprietary wetting agent, such as for example: Tenlo 70, manufactured by Nopco Chemical Company.

A third general form of treatment which may be employed for reducing the emulsification tendencies of magnetic pigments such as those listed above, is to treat the pigment with chemically reactive materials giving rise to phosphatizing, nitrating and other surface reactions on the pigment particles which will provide roughened pigment particle surfaces and improved pigment particle hydrophobicity. Such treatments will result in improved wetting of pigment particles by the resins in an ink formulation. Such processes are well known in the art and need not be described in detail herein.

Following is an example of an ink formulation embodying pigment particles treated by the third form of treatment described above:

68 gms. phosphatized natural magnetite, reduced in particle size to under 5 microns average.

10 gms. bodied China-wood oil, Gardner bubble tube. Viscosity: Z 5½ at 77° F.

35 9 gms. 100% solids isophthalic alkyd varnish, Gardner bubble tube viscosity Z 2½ at 70° F.

8 gms. black colorant, consisting of 20 parts impingement black, particle size 24 millimicrons, flushed into #0 and #3 bodied linseed oils.

40 2 gms. 21% cobalt drier.

3 gms. paraffin oil, light. Viscosity: 125/135.

A fourth general form of treatment which may be employed for reducing the emulsification tendencies of magnetic pigments, such as those listed above, involves mixing the pigments with suitable surface active agents. Suitable surface active agents such as those set forth in the following examples may be either mixed directly with the dry magnetic pigment or, preferably may be dissolved in a solvent into which the magnetic pigments are stirred, whereupon the solvents are evaporated off, leaving the pigment particles coated with the surface active agent. The use of the solvent coating technique provides improved uniformity of coating. Certain surface active agents are then desirably treated to improve their effectiveness in reducing the hydrophilicity of the pigment particles. The following are examples of surface active agent treatments:

Example 1

5% by weight ricinoleic acid mixed with 95% by weight of a ferric iron oxide magnetic pigment such as IRN-100. While the ricinoleic acid is preferably mixed with a solvent such as heptane B, the mix may be made in dry powder form. After the materials are thoroughly mixed and, if solvent is used, the solvent driven off, the coated magnetic particles are employed as pigment in a suitable magnetic ink formulation such as numerous formulations well known in the art.

Example 2

3 grams of a surfactant comprising a 5 to 1 mixture of dialkyl quaternary ammonium chloride and an ethoxylated amine acetate is mixed with 97 grams of a ferric oxide such as IRN-100 by first dissolving the surfactant

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in warm water and then adding the solution to a loose slurry of the iron oxide in water. The resultant slurry is stirred for 10 to 15 minutes and then 20 cc. of a 1% NaOH solution is added to this slurry with continued stirring for an additional 15 minutes. There results a molecular interchange providing a strongly bonded coating on each pigment particle. Thereafter the slurry is filtered and the filtrate is washed and dried. The coated pigment filtrate may then be used in a conventional magnetic lithographic ink formulation.

Further examples of surface active agents which may be employed are: organic aluminum compounds, oil soluble non-ionic ammonium surfactants, and other applicable anionic and cationic surfactants.

Following is an example of an ink formulation embodying pigment particles treated by the fourth form of treatment described above:

- 55 gms. gamma ferric oxide particle size .3 x 2 microns average, exemplified by IRN-100 pigment, coated with 5% ricinoleic acid, as described above.
- 17 gms. heavy body 100% solids isophthalic alkyd varnish, viscosity Z 7½ on Gardner tube.
- 10 gms. loose body 100% solids isophthalic alkyd varnish, viscosity Z 2½, at 77° F. on Gardner tube.
- 8 gms. black colorant base, consisting of 20 parts by weight of impingement carbon black, particle size 24 millimicrons, flushed into #0 and #3 bodied linseed oil.
- 5 gms. blue toner, consisting of 41 parts by weight prussian alkali blue in linseed oil.
- 4 gms. paraffin oil, light. Viscosity: 125/135.

From the foregoing, it will be evident that various methods may be employed for treating magnetic pigment particles for reducing emulsification tendencies of lithographic ink brought about by the hydrophilicity of magnetic pigment particles. It will also be evident to one skilled in the art of compounding lithographic inks that magnetic pigment particles treated in accordance with the foregoing, may be employed in numerous ink formulations and that any given formulation will be dependent upon the conditions of lithographic printing that the ink must satisfy. For example, ink formulations are influenced by the nature of the printing plate, the nature and the work surface on which the printing is ultimately accomplished, the particular printing characteristics desired, i.e., sharpness, color depth, etc., and numerous other considerations well known to those skilled in the lithographic printing art. The invention disclosed herein, however, is applicable to a great variety of lithographic printing applications and it will be evident to one skilled in the art that the various methods by which the pigment particles may be coated may be selectively employed depending upon other considerations involved in the com-

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pounding of a particular ink for a particular purpose without departing from the scope of the invention as set forth in the following claims.

What is claimed is:

1. An oleophilic lithographic ink consisting essentially of a minor proportion of an oleophilic ink vehicle and a major proportion of a magnetizable hydrophobic pigment, said pigment consisting of normally hydrophilic magnetizable particles having a largest dimension of 10 microns or less and a relatively thin coating deposited on said particles, said coating having an external surface which is substantially hydrophobic and wettable by said vehicle whereby a magnetizable water-repelling ink is provided.
2. A lithographic ink as recited in claim 1 in which said coating is a resinous material selected from the class consisting of melamine resins, cyclized rubber, silicenes, vinyl chloride, chlorinated paraffines and zein.
3. A lithographic ink as recited in claim 1 in which said coating is a dyestuff having a molecular chain with one end portion of a hydrophilic nature attached to said particle and the other end portion is of an oleophilic nature.
4. A lithographic ink as recited in claim 1 in which said coating is a surface active agent selected from the class consisting of ricinoleic acid, organic aluminum compounds, oil soluble non-ionic ammonium surfactants and the reaction product of a mixture of di-alkyl quaternary ammonium chloride and an ethoxylated amine acetate with sodium hydroxide.
5. An ink as recited in claim 3 in which said coating is a rhodamine tungstate-molybdate dye.

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