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MAGNETIC LITHOGRAPHIC INK

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6 Claims. (Cl. 252—62.5)

This invention relates to magnetic inks for use in lithographic duplication to produce copies capable of read-out with the magnetic reading head in automatic, high-speed scanning devices. It relates more particularly to a lithographic duplicating ink embodying characteristics essential for lithographic duplication and which embodies a magnetic component to produce copies having magnetic properties for use with magnetic read-out devices. In a specific embodiment, it is concerned with magnetic pigments and/or components for lithographic inks which are hydrophobic in character and are completely compatible with the components used to prepare lithographic ink formulation.

In our copending application Serial No. 767,093 for "Magnetic Lithographic Ink" filed October 14, 1955, it is disclosed that when magnetic iron oxide is used in lithographic inks, valuable magnetic lithographic ink compositions are provided. When care is exercised in selecting the ingredients used in preparing these inks and careful attention is given to their formulation, excellent magnetic lithographic inks are produced.

It has sometimes been experienced that the magnetic iron oxide component of such inks, due to its hydrophilic character, produces lithographic ink formulas which will feed back into the fountain solution. It is also noted that occasionally the ink will tend to back away from the rolls. These occurrences may often be traced to the improper blending techniques used to prepare the formulations and in some instances it has been found to occur when off-grade specification ingredients are employed.

It would be a valuable contribution to the art if a magnetic lithographic ink formulation were available which could be easily prepared and which would not be subject to such objectionable characteristics as fountain bleed or roll back-off.

It is an object of this invention to produce a magnetic ink having lithographic properties for use in lithographic duplicating machines to produce magnetic printing, and it is a related object to produce a lithographic ink of the type described; which contains a magnetic component in the form of a magnetic iron oxide; which produces easily readable and well defined copy; which does not feed back into the fountain solution of the lithographic duplicating machines thereby to keep the fountain free of contaminating magnetic particles; which produces copy having sufficient magnetic strength for efficient and proper read-out, and which is capable of producing a large number of copies of good quality.

In accordance with the practices of this invention, it has been found that improved magnetic inks may be prepared by using, as the magnetic component, a magnetic iron oxide which has been rendered hydrophobic by coating its surface with certain organic compounds. These organic coated iron oxide materials, for purposes of generally defining the invention, will hereinafter be referred to as "hydrophobic magnetic iron oxide."

The concepts of this invention may be represented by reference to the following lithographic ink formulation which is given by way of illustration and not by way of limitation:

GENERAL FORMULA

Ingredients:	Percent by weight
Lithographic vehicle or varnish—	
General range	20–60
Preferred range	20–45
Hydrophobic magnetic iron oxide—	
General range	25–75
Preferred range	45–60
Toners—	
General range	0–20
Preferred range	1–5
Surface active agents—	
General range	0–20
Preferred range	1–5

Lithographic ink varnishes are well known to the trade. They usually comprise a base capable of fluid flow. The base may be a bodied oil, such as linseed oil, or a liquid hydrocarbon, or an oil modified synthetic resinous material such as alkyd resin or a phenol formaldehyde resin. The following are classes of varnishes which can be used:

Linseed modified phenol formaldehyde varnish
Bodied linseed oil varnish
Maleic-alkyd varnish
Pentaerythritol alkyd varnish
Hydrocarbon varnish

It is preferred to make use of a lithographic varnish giving a high degree of water repellency to the copy. A suitable varnish is marketed by General Printing Ink Company under the designation No. 01269.

The toner comprises a tinctorial agent to impart a desired color and readability to the copy. It will be apparent that, in magnetic read-out, a toner will be unnecessary. Thus, the invention contemplates an ink composition with or without toner. The presence of a toner is preferred, however, for purposes of proof-reading or correction. When present, use can be made of such conventional toners as carbon black, lamp black, alkali blue, iron blue, and other dyestuffs and pigments. They may be incorporated as a dry pigment or as a dispersion in varnish oils for introduction into the composition.

The surface active agent functions also as a wetting agent for the pigment. For this purpose, best use can be made of a lecithin or other hydrophilic colloid such as algin, gums, etc. A suitable material (soy bean lecithin) is marketed by American Lecithin Company, Long Island City, New York, under the trade name "ALCOLEC HO #410–N."

The hydrophobic magnetic iron oxides are prepared by coating a finely divided magnetic iron oxide with an organic compound which contains at least one acyclic group of at least 6 carbon atoms in chain length. While any particular finely divided iron oxide may be used, it is preferred to use a special grade of iron oxide identified as acicular iron oxide which is prepared from commercial grades of iron oxide by known reduction and oxidation techniques. A commercially available iron oxide of this type is the material IRN100 marketed by C. K. Williams Company of Easton, Pennsylvania.

The organic compounds containing at least one acyclic group of at least 6 carbon atoms in chain length are preferably selected from the class of organic aliphatic carboxylic acids, such as fatty acids of at least 6 carbon atoms in chain length. While it is important that the particular fatty acids selected contain at least 6 carbon atoms in an aliphatic arrangement, fatty acids containing as many as 20 or more carbon atoms may also be used. In a preferred practice of this invention, it is desirable to use fatty acids which contain from 12–18 carbon atoms in chain length. While pure grades of fatty acids may be used, it is contemplated that mixtures of fatty acids, such as those commonly occurring in vegetable oils and animal fats may also be employed. Illustrative fatty acids capable of being used to prepare the hydrophobic iron oxides are such acids as: capric, caprylic, capric, lauric, myristic, palmitic, stearic, arachidic, behenic, lignoceric, lauroleic, myristoleic, palmitoleic, oleic, gadoleic, erucic, ricinoleic, linoleic, linolenic, eleostearic, licanic, arachidonic and clupanodonic. Of the above fatty acids, the most useful hydrophobic magnetic iron oxides have been produced using lauric acid.

In addition to those fatty acids described above, the fatty acids derived from the following vegetable oils and animal fats may be employed with good results being obtained in each instance: babassu, castor, coconut, corn, cottonseed, linseed, olive, oiticica, palm, palm kernel, peanut, perilla, rapeseed, safflour, sesame, soybean, tall (commercial), tung, lard, neatsfoot, tallow (beef), tallow (mutton), herring, menhaden, sardine, sperm (body), sperm (head), and whale.

While the fatty acids described above are iminently suited for producing the hydrophobic magnetic iron oxides used in preparing the magnetic lithographic inks, it has also been found that the fatty acids may be substituted either in whole or in part by other specific organic compounds which contain at least one acyclic group of at least 6 carbon atoms in chain length. For instance, aliphatic substituted quaternary ammonium salts, aliphatic amines, aliphatic amides and ethoxylated alkyl substituted amines may also be used.

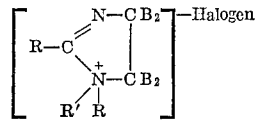
The quaternary ammonium salts may be either aliphatic or they may be heterocyclic. The aliphatic quaternary ammonium salts are preferred members of this group. Regardless of the specific type quaternary ammonium salt selected, it is desirable that it contain from one to two higher aliphatic groups of from 12–18 carbon atoms in chain length. It will be understood that those quaternary ammonium salts having aliphatic substituents ranging from 6–12 carbon atoms may also be employed. Typical aliphatic quaternary ammonium salts are the higher fatty substituted quaternary ammonium salts which are sold by the Armour Chemical Company under the trade name "Arquads." They include such compounds as soya-trimethyl ammonium chloride, disoya dimethyl ammonium chloride, dicoconut dimethyl ammonium chloride, dihydrogenated tallow dimethyl ammonium chloride, tallow trimethyl ammonium chloride, dodecyl trimethyl ammonium chloride, hexadecyl trimethyl ammonium chloride and octyldecyl trimethyl ammonium chloride. Of the above materials, excellent results have been obtained with disoya dimethyl ammonium chloride.

A heterocyclic higher alkyl substituted quaternary ammonium salt that may be used to prepare the hydrophobic magnetic iron oxides are exemplified in a preferred embodiment by the higher 2-substituted imidazolinium salts. These imidazolinium salts are conveniently prepared by alkylating, with a suitable alkyl halide, an imidazoline formed by the reaction of an ethylene polyamine with a fatty acid for the elimination of 2 mols of water.

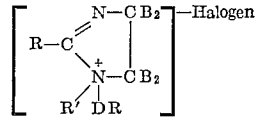
Starting 2-substituted imidazolines from which the imidazolinium salts are prepared are described in Wilson U.S. Patents 2,267,965 and 2,355,837. Typical formulas

of the imidazolinium salts of the type generically described above are presented below:

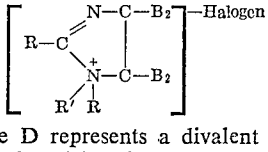
FORMULA 1



FORMULA 2



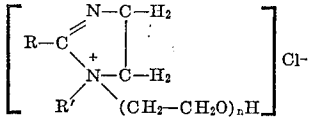
FORMULA 3



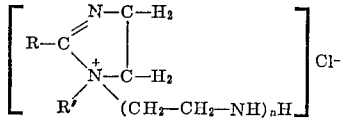
In the above D represents a divalent organic radical containing less than 25 carbon atoms, composed of elements from the group consisting of C, H and O, and containing at least 1 amino group; R is a member of the class consisting of hydrogen and aliphatic and cycloaliphatic hydrocarbon radicals, with the proviso that at least 1 occurrence of R contains 6 to 20 carbon atoms. R′ is a member of the class consisting of aliphatic, haloaliphatic, aralkyl and halosubstituted aralkyl radicals. R′ preferably contains from between 2 to not more than 12 carbon atoms. B is a member of the class consisting of hydrogen and alkyl radicals, having not over 2 carbon atoms, with the proviso that at least 3 occurrences of B be hydrogen.

A preferred class of 1, 2-substituted imidazolium salts may be depicted by the following general formulas:

FORMULA 4



FORMULA 5



R above is an aliphatic group of at least 6 carbon atoms in chain length, R′ is from the group consisting of aliphatic and halosubstituted aliphatic groups of not more than 6 carbon atoms in chain length and *n* is a small whole number.

Additional imidazolium salts which contain two or more higher acyclic groupings are further disclosed in Carl E. Johnson, U.S. Patent 2,874,074, the disclosure of which is incorporated herein by reference.

Another useful group of organic compounds that may be utilized in preparing the hydrophobic magnetic iron oxides are the higher aliphatic amines which have been reacted with from 2 mols to 50 mols of ethylene oxide. Commercially available compounds of this type are the alkyl amines which are made available by Armour Chemical Company. These products include such materials as soya amine reacted with 50 mols of ethylene oxide, cocoamine reacted with 5 mols of ethylene oxide, soyamine reacted with 15 mols of ethylene oxide, oleoamine reacted with 15 mols of ethylene oxide, tallowamine reacted with 5 mols of ethylene oxide and lauroamine reacted with 2 mols of ethylene oxide. The alkyl group should contain at least 6 and preferably 12–18 carbon atoms.

In order to effectively coat the magnetic iron oxide with compounds which contain a primary, secondary, or

tertiary amino group, it is oftentimes desirable to use the amine compounds in the form of its acid salt. This is very beneficial when the ethoxylated amines of the type just described are used. A particularly useful ethoxylated amine is the acetic acid salt of soyamine which has been reacted with 2 mols of ethylene oxide thereby producing the compound N-soya di-(2-hydroxy ethyl) amine acetate.

Another useful group of organic compounds capable of rendering magnetic iron oxide hydrophobic are the higher alkyl amides which contain at least 6 carbon atoms in chain length and preferably from 12–18 carbon atoms in chain length. Materials of this type are exemplified by such compounds as the N-cocoamide, N-octyldecylamide, and N-hydrogenated tallow amide. These amides are available commercially from Armour Chemical Company under the trade name of "Armids."

In addition to using the alkyl monoamides, it is possible to use the amides produced by reacting a fatty acid of at least 6 carbon atoms in chain length with a polyamine. The polyamine may be represented by ethylene diamine, hexamethylene diamine, diethylene triamine, tetraethylene pentamine and the like. Exemplary compounds of this class are such materials as N,N' dioleyl ethylene diamine, N,N' distearyl ethylene diamine, the reaction product of 2 mols of lauric acid with one mol of tetraethylene pentamine.

To prepare the hydrophobic magnetic iron oxides from the organic chemicals thus described, a number of techniques may be employed. A simple method of coating the organic compound onto the surface of the magnetic iron oxide particles is to form a treating bath comprising an aqueous solution, slurry or suspend the organic compound in a polar solvent such as water or lower aliphatic alcohol such as methanol, ethanol, isopropanol and the like. The magnetic iron oxide is then added to the polar solvent-organic compound treating bath. After a sufficient contact with the reagents in the bath the magnetic iron oxide is removed and treated either by filtration, centrifuging or decantation. The treated iron oxide, if filtered, is removed as a filter cake and allowed to dry either at ambient atmospheric temperature or at elevated temperatures to remove all traces of polar solvent from the filter cake. After the magnetic iron oxide has been dried, it is ready for incorporation into the lithographic ink formulation to produce a magnetic lithographic ink.

The amount of organic compound coated on the surface of the magnetic iron oxide to render it hydrophobic need only be sufficient to produce a monomolecular surface layer. While such amounts are small, it is contemplated that thicker layers may also be built up on the surfaces of the magnetic iron oxide without departing from the spirit of the invention. Thus layers as thin as several angstrom units to as thick as several microns may be placed upon the magnetic iron oxide to render it hydrophobic. The amount of organic compound contained in the treating bath will be in excess of the amount actually coated upon the iron oxide since a portion of the organic compound will remain in the treating solution. Thus, it is possible to employ the organic compound in polar solvent in amounts ranging from .001 percent to as high as 5 percent by weight. For an illustration of a typical procedure used in coating the magnetic iron oxide with the organic compound to produce a hydrophobic iron oxide of the invention, the following are presented by way of examples:

Example 1

100 grams of iron oxide (IRN100) was slurried into 1.8 percent solution of lauric acid in ethanol. After the magnetic iron oxide had been completely contacted by the lauric acid solution, it was removed therefrom and dried at ambient temperature for two days to completely remove any trace of solvent.

Example 2

100 grams of magnetic iron oxide (IRN100) was slurried into 3.1 percent solution of disoya dialkyl dimethyl ammonium chloride. After contacting the solution for 20 minutes, the magnetic iron oxide was dried at a temperature of 240° F. for six hours to remove any traces of water.

Example 3

100 grams of magnetic iron oxide (IRN100) was slurried into a 0.6 percent solution of N-soya di-(2-hydroxyl ethyl) amine acetate. After contacting the solution for 20 minutes, the magnetic iron oxide was separated therefrom and dried at a temperature of 240° F. for 6 hours to remove any traces of water.

Example 4

100 grams of magnetic iron oxide (IRN100) was slurried into a solution containing 3.1 percent of disoya dimethyl ammonium chloride and 0.6 percent solution of N-soya di-(2-hydroxyl ethyl) amine acetate. After contacting this solution for 20 minutes, the magnetic iron oxide was removed by filtration and dried at a temperature of 240° F. for 6 hours to remove all traces of water.

Example 5

100 grams of magnetic iron oxide (IRN100) was slurried into a 0.5 percent by weight suspension of stearmide in water. After contacting the stearmide suspension for 20 minutes, the magnetic iron oxide was dried at a temperature of 240° F. for 6 hours to remove all traces of the water.

Illustrative magnetic lithographic ink formulations prepared from the hydrophobic magnetic iron oxides of the type described above are presented below by way of further illustration:

Example 6

	Percent
P. E. Alkyd varnish	37
Linseed oil	10
Lecithin	1
Carbon black	1
Iron blue	1
Hydrophobic magnetic iron oxide of Example 2	50
	100

Example 7

	Percent
Maleic alkyd varnish	44
Alkali blue	1
Lamp black	2
Hydrophobic magnetic iron oxide of Example 3	53
	100

Example 8

	Percent
Linseed oil varnish	32
Alkali blue	2
Linseed oil	16
Hydrophobic magnetic iron oxide of Example 4	50
	100

Example 9

	Percent
Linseed modified phenolic varnish	27
Linseed oil	15
Hydrophobic magnetic iron oxide of Example 1	56
Lecithin	1
Alkali blue	1
	100

Example 10

	Percent
Water repellent varnish	26
Raw linseed oil	14
Soybean lecithin	1
Flushed alkali blue	3
Hydrophobic magnetic iron oxide of Example 1	56
	100

The materials may be incorporated in any order but it is best to mix all of the ingredients and then grind the formula in conventional machines for the preparation of lithographic inks.

The magnetic lithographic inks of the type illustrated not only have freedom from fountain bleeding and ink backoff but they tend also to have better body and other physical and chemical characteristics which make them far superior in the use of reproduction of copy when used in offset duplication processes. Since the magnetic iron oxides are hydrophobic, they blend more easily with the other components of the formulation thereby providing greater stability from the standpoint of storage and use.

The expressions "magnetic component" or "magnetic pigment" or "component" or "pigment" for purposes of this disclosure are used interchangeably throughout the specification and claims and are considered as being synonymous when used to describe the hydrophobic magnetic iron oxides.

Having thus described our invention in all its useful and novel aspects, it is claimed as follows:

We claim:

1. A magnetic lithographic ink comprising the combination of 20–45 percent by weight varnish, 1–5 percent by weight tinctorial agent, 1–5 percent by weight surface active agent and 45–60 percent by weight of a magnetic iron oxide which contains a surface coating selected from the group consisting of a quaternary ammonium salt having at least one acyclic group containing at least 6 carbon atoms in chain length, an ethoxylated amine having at least one acyclic group containing at least 6 carbon atoms in chain length, and an amide having at least one acyclic group containing at least 6 carbon atoms in chain length.

2. The magnetic lithographic ink of claim **1** where the surface active agent is lecithin.

3. The magnetic lithographic ink of claim **1** wherein the surface coating is a quaternary ammonium salt which contains at least one aliphatic group which is a mixed aliphatic group of the type occurring in vegetable oils and animal fats.

4. The magnetic lithographic ink of claim **3** wherein the surface coating is disoya-dimethyl ammonium chloride.

5. The magnetic lithographic ink of claim **1** wherein the surface coating is soya amine which has been reacted with 2 mols of ethylene oxide and is in the form of its acetate salt.

6. The magnetic lithographic ink of claim **1** wherein the surface coating is stearamide.

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