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3,266,914

NOVEL PRINTING INKS AND METHOD OF PRINTING WITH SAID INKS

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This invention relates to printing inks and a method of printing therewith useful in the printing of newspapers, telephone books, comic books, paper back books and similar porous stocks conventionally known as "newsprint" stock. More particularly, this invention is directed to the production of "water-in-oil" emulsion type of inks for printing on "newsprint" stock which display considerably less excessive penetration to stain the reverse side of the stock or "strike-through" than do the conventional "newsprint" inks which employ the ink-oil vehicles. In addition, the inks of this invention give greater clarity and sharpness in the outlines of the printed matter particularly in the case of halftones which are usually quite difficult to produce with conventional newsprint inks.

It should be noted that the problem of "strike-through" and less than desirable clarity of printing are problems that the art of "newsprint" printing has been continuously trying to overcome. Those in the art have used various methods in solving these problems, for example the well known heat-setting printing techniques as set forth in U.S. Patents 2,087,190, 2,285,430, 2,301,854 and 2,579,836. While heat-setting printing does provide improved clarity of printing and less "strike-through" than do the conventional newsprint printing methods, it also necessitates an additional heating step after printing as well as the use of auxiliary press equipment for such heating.

The ink and method of this invention now provide improved clarity of printing and substantial reduction of strike-through without the necessity of heating and heating equipment. The printed matter is preferably maintained at ambient temperature.

In accordance with this invention, there is provided a printing ink comprising pigment dispersed in a vehicle comprising water emulsified in a water-immiscible ink vehicle liquid by a monoglyceride of oil fatty acid, preferably drying oil fatty acid. Best results have been obtained when either the monoglyceride of tall oil fatty acid or glyceryl monooleate are used. However other monoglycerides such as safflower oil fatty acid, soyabean oil fatty acid, cotton seed oil fatty acid and coconut oil fatty acids give satisfactory results.

According to one aspect of this invention, the water-immiscible ink vehicle in which the water is emulsified by the above described monoglycerides is the ink-oil or mineral oil used in conventional newsprint inks. Likewise conventional heat-setting ink vehicles may be used as the continuous phase in the emulsion inks of this invention. These heat-setting ink vehicles conventionally comprise a solution in a predominantly paraffinic hydrocarbon solvent, preferably having a boiling range of 425–650° F., of a thermoplastic resin soluble therein. Among the resins conventionally used in these vehicles are limed and zincated rosins, hydrocarbon resins such as petroleum residue resins, modified phenolics such as rosin modified phenolics, coal tar resins, asphalt, rosin glycerol esters and rosin pentaerythritol esters.

It is to be noted that in the specification and claims herein, all proportions are by weight unless otherwise stated. Preferably, the water content based upon the vehicle weight is from about 10 to about 70% and most preferably from 25 to 60%. The monoglyceride of oil

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fatty acid preferably comprises from 1.0 to 5.0% of the vehicle weight.

It has been further found that the addition of small quantities of the sodium salt of petroleum sulfonate may be used to improve the flow properties of the inks of this invention. When used, said sodium salt is added in quantities preferably equal to from about 1.0 to 6.0% of the vehicle weight.

It has been found that colloidal magnesium aluminum silicate improves the stability of the emulsion inks to some extent and in some cases improves the transfer properties of said inks. When used said colloidal silicate is added in quantities preferably equal to from about 0.25 to 2.0% of the vehicle weight.

In both printing in black or in color as for comics, the conventional "newsprint" pigments may be used in conventional quantities in the ink formulation.

The following examples will further illustrate the practice of this invention.

Example 1

Thirty parts of chrome yellow pigment are dispersed in 20 parts of mineral oil. Then 47 parts of water and 3 parts of the monoglyceride of tall oil fatty acid are added and the mixture is stirred on a high speed stirrer until the water is dispersed in the mineral oil. The quantities of pigment and monoglyceride are held constant while the example is repeated using the following proportions of water and mineral oil.

Water.....	37	27	17	0
Mineral Oil.....	30	40	50	67

The five resulting inks are used in printing upon newsprint stock which is air dried. The ink containing no water rapidly penetrates into the stock and in a few hours the oil migrates through to the back of the sheet and transparentizes the stock causing substantial "show-through." In contrast, the other "water in oil" emulsion inks show little or no show-through or oil migration to the back of the sheet even several months after the printing. In addition, all of the water in oil inks show improved sharpness in printing over the waterless ink, with the sharpness improving with increased water content, and display a rub resistance equivalent to that of the waterless inks.

Example 2

Example 1 is repeated using 30 parts of chrome yellow pigment, 20 parts of mineral oil, 47 parts of water and 3 parts of the monoglyceride of tall oil fatty acid and further including, in the mineral oil, 1.5 parts of the sodium salt of petroleum sulfonate, having an average molecular weight of 440 (petroleum sulfonate is made by the treatment of lubricating oil distillates with fuming sulfuric acid). The resulting ink has properties equivalent to the high water content ink of Example 1 and further displays slightly improved flow properties.

Example 3

Example 1 is repeated using 30 parts of chrome yellow pigment, 20 parts of mineral oil, 47 parts of water and 3 parts of tall oil fatty acid monoglyceride and further including 0.6 part of colloidal magnesium aluminum silicate sold commercially as "Veegum." The resulting ink has properties equivalent to the high water content ink of Example 1 and further displays slightly better transfer properties.

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Example 4

Example 1 is repeated using 30 parts of water, 50 parts of mineral oil, 14 parts of blue pigment consisting of an equal mixture of iron blue and peacock blue and 4 parts of cocoanut oil fatty acid monoglyceride. The resulting ink has properties equivalent to that of Example 1 except that sharpness in printing is about the same as the ink containing 27 parts of water.

Example 5

Example 4 is repeated using the same ingredients, proportions and conditions except that the monoglyceride is safflower oil fatty acid monoglyceride. The resulting ink has properties equivalent to that of Example 4.

Example 6

Example 4 is repeated using the same conditions, ingredients and proportions except that the monoglyceride is soya bean oil fatty acid monoglyceride. The resulting ink has properties equivalent to that of Example 4.

Example 7

Example 4 is repeated using the same conditions, ingredients and proportions except that the monoglyceride is cotton seed oil fatty acid monoglyceride. The resulting ink has properties equivalent to that of Example 4.

Example 8

Example 1 is repeated using the following composition:

	Parts
Carbon black pigment	12.7
Mineral oil	52.3
Water	29.6
Glyceryl monooleate	3.0

The resulting ink has the same properties as the inks of Example 1 with a sharpness in printing equivalent to the ink containing 27 parts of water.

Example 9

10 parts of lithol red pigment are dispersed in 57 parts of a varnish comprising 37.5% Pentalyn G resin (pentaerythritol ester of resin condensed with 5% maleic anhydride) and 62.5% of a substantially paraffinic hydrocarbon solvent having a boiling range of from 500 to 525° F. and a K.B. value of from 24 to 27. Then 30 parts of water and 3 parts, of the monoglyceride of tall oil fatty acid are added and the mixture is stirred on a high speed stirrer until the water is dispersed in the varnish. The resulting ink is used in printing upon newsprint stock. The ink has slightly improved rub resistance over the inks of Example 1. The other properties of this ink are the same as the inks of Example 1 including a sharpness in printing at least equivalent to the ink of Example 1 which contains 47 parts of water.

Example 10

12 part of carbon black pigment are dispersed in 53.5 parts of a varnish comprising a 32.3% solution of Pentalyn K resin (pentaerythritol ester of rosin dimer) in a substantially paraffinic hydrocarbon solvent having a boiling range of 480 to 536° F. and a K.B. value of 26. Then 30 parts of water, 2 parts of glyceryl monooleate and 2 parts of the monoglyceride of soyabean oil fatty acid are added and the mixture is stirred on a high speed stirrer until the water is dispersed in the varnish. The resulting ink is used in printing upon newsprint stock. The ink has slightly improved rub resistance over the inks of Example 1. The other properties of this ink are the same as the inks of Example 1 including a sharpness in printing at least equivalent to the ink of Example 1 which contains 47 parts of water.

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Example 11

Example 10 is repeated using the following:

	Parts
Carbon black	12
38.8% solution of 6% limed rosin in an aliphatic solvent (boiling range 480 to 536° F., K.B. 26)	55
Glyceryl monooleate	2
Monoglyceride of soyabean oil fatty acid	2
Water	30

The resulting ink has the same properties as that of Example 10.

The following examples are carried out following the procedure of Examples 10 and 11. The inks produced display the same desirable properties as those of Examples 10 and 11:

Example 12

	Parts
Carbon black	12
25% solution of Utah coal resin in an aliphatic solvent (boiling range 480 to 536° F., K.B. 26)	52
Glyceryl monooleate	2
Monoglyceride of soyabean oil fatty acid	2
Water	30

Example 13

	Parts
Carbon black	12
33.3% solution of a 1:1 blend of gilsonite and 6% limed rosin in an aliphatic solvent (boiling range 480 to 536° F., K.B. 26)	52
Glyceryl monooleate	2
Monoglyceride of soyabean oil fatty acid	2
Water	30

Example 14

	Parts
Carbon black	12
36.5% solution of a zincated limed rosin which has a zinc content of 7.0% and a lime content of 3.1% in an aliphatic solvent (boiling range 480 to 536° F., K.B. 26)	55
Glyceryl monooleate	2
Monoglyceride of soyabean oil fatty acid	2
Water	30

As one of the primary requisites of the emulsion inks of this invention is stability both "on the shelf" and during the actual printing operation on the newsprint stock, the ink vehicles of this invention were compared to vehicles produced by using a variety of emulsifying agents conventionally used in water-in-oil emulsions in place of the monoglycerides of this invention in the same vehicles as the inks of this invention.

The vehicles resulting from the use of these conventional agents were significantly less stable than the vehicles of this invention. In fact, the stabilities were such that the vehicles were unsatisfactory for printing on newsprint in accordance with the method of this invention. Among the conventional emulsifying agents so evaluated and found to be lacking in stability were mono-fatty acid esters of polyoxyethylene glycols such as the mono-cocoanut oil fatty acid ester of polyoxyethylene glycol; anionic surfactants such as sodium heptadecyl sulfate; fatty amines such as hexadecylamine, octadecylamine and octadecenylamine; quaternary ammonium salts from fatty amines such as alkyl trimethylammonium salts wherein the alkyl groups may be hexadecyl, octadecyl, octadecenyl and octadecadienyl groups; the acetic acid salts of the above described fatty amines; N,N-substituted fatty amines of the type described above such as octadecylamine, N,N-substituted by $(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ groups and having a molecular weight of 495; and N,N-substituted fatty acid amides such as hydrogenated tallow amide substituted by $(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ groups and having a molecu-

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lar weight of from 500 to 2500. Further, when the inks of this invention are used as "comic inks" for the printing of comics, it is necessary for the emulsifying agent to be wholly unreactive with the colors. The monoglyceride type of emulsifying agents used in this invention are unreactive with the colored pigments used in comic inks. On the other hand, the aforementioned fatty amines, substituted fatty amines, fatty amides and salts of fatty amines have been found to react with pigment used in comic inks such as barium lithols, calcium lithols, phloxine reds and peacock blue to cause discoloration and loss of color strength.

While there have been described what is at present considered to be the preferred embodiments of this invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention, and it is, therefore, aimed to cover all such changes and modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. A printing ink comprising coloring matter dispersed in a vehicle comprising water emulsified in a water-immiscible ink vehicle liquid selected from the group consisting of mineral oil and solutions of limed rosin, rosin glycerol esters, rosin pentaerythritol esters, petroleum residue resins, coal tar resins, asphalt and rosin modified phenolic resins in paraffinic hydrocarbon solvents by monoglycerides of oil fatty acids.

2. The ink of claim 1 wherein said monoglyceride is the monoglyceride of drying oil fatty acids.

3. The ink of claim 2 wherein said monoglyceride is the monoglyceride of tall oil fatty acid.

4. The ink of claim 2 wherein said monoglyceride is glyceryl monooleate.

5. The ink of claim 1 wherein said water-immiscible ink vehicle liquid is mineral oil.

6. The ink of claim 1 wherein said vehicle is a solution of rosin pentaerythritol esters in a paraffinic hydrocarbon solvent.

7. The ink of claim 6 wherein said solvent has a boiling range from 425° to 650° F.

8. The ink of claim 1 wherein said vehicle is a solution of limed rosin in a paraffinic hydrocarbon solvent.

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9. The ink of claim 1 wherein said vehicle is a solution of coal tar resins in a paraffinic hydrocarbon solvent.

10. The ink of claim 1 further including colloidal magnesium aluminum silicate.

11. The ink of claim 1 further including the sodium salt of petroleum sulfonate.

12. A method of printing on newsprint stock which comprises applying to said newsprint stock coloring matter dispersed in a vehicle comprising water emulsified in a water-immiscible ink vehicle liquid selected from the group consisting of mineral oil and solutions of limed rosin, rosin glycerol esters, rosin pentaerythritol esters, petroleum residue resins, coal tar resins, asphalt and rosin modified phenolic resins in paraffinic hydrocarbon solvents by monoglycerides of oil fatty acids and drying said printed stock at ambient temperatures.

13. The method of printing of claim 12 wherein said monoglyceride is the monoglyceride of drying oil fatty acid.

14. The method of claim 12 wherein said monoglyceride is the monoglyceride of tall oil fatty acid.

15. The method of printing of claim 12 wherein said monoglyceride is glyceryl monooleate.

16. The method of printing of claim 12 wherein said water-immiscible ink vehicle liquid is mineral oil.

17. The method of a printing of claim 12 wherein said solvent has a boiling range from 425° to 650° F.

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