(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 June 2001 (14.06.2001)

PCT

(10) International Publication Number
WO 01/42377 A1

(51) International Patent Classification[7]: C09D 11/10

(21) International Application Number: PCT/CA00/01462

(22) International Filing Date: 7 December 2000 (07.12.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/455,762 7 December 1999 (07.12.1999) US

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/42377 A1

(54) Title: INTAGLIO PRINTING INKS HAVING IMPROVED DISPERSIBILITY AND CHEMICAL RESISTANCE

(57) Abstract: Intaglio printing inks having both improved dispersibility and chemical resistance are provided and, in particular, dispersibility in tap water is provided. The ink comprises an alkyd containing an unsaturated oily component, an anionic or nonionic surfactant and an organic base selected from the group consisting of alcohol-amines, ring-containing nitrogen compounds and substituted polyethyleneimines, wherein the substituted polyethyleneimines are modified with epichlorohydrine or alkoxylated and the organic base has a boiling point higher than 150 °C. Alternatively, a zwitterionic surfactant may be used in which case an cxorganic base is not separately included. The ink may also comprise water.

TITLE OF THE INVENTION

INTAGLIO PRINTING INKS HAVING IMPROVED DISPERSIBILITY AND CHEMICAL RESISTANCE

FIELD OF THE INVENTION

The invention is in the field of intaglio printing inks having improved dispersibility and chemical resistance.

BACKGROUND OF THE INVENTION

Intaglio printing is typically used for printing security documents, such as banknotes, and uses printing cylinders having engravings therein in which intaglio printing inks have been deposited. The ink is applied to the printing cylinder so as to fill the engravings and then the excess ink on the cylinder (i.e., the ink which is outside of the engravings) is typically removed by a wiping cylinder which wipes off the excess ink. A diluted aqueous solution of sodium hydroxide, i.e. an alkaline (caustic) solution, is normally used by the wiping cylinder to emulsify and remove the excess ink. Therefore, in order to achieve effective wiping of the printing cylinders, it is important that the ink readily disperses in the wiping solution.

The poor dispersibility of known commercial inks in the alkaline washing solutions used in the cylinderwipe intaglio printing processes is often a problem and, to deal with this problem, attempts are often made to improve dispersibility by adding surfactants to the ink. However, the addition of surfactants usually results in a rapid loss of resistance to solvents and chemicals, particularly at higher surfactant concentrations, such as 2 - 10 weight%.

Disadvantageously, when using a caustic wiping solution it is necessary to have ultrafiltration equipment to recover caustic values from the washing solution containing the suspended inks and extra chemicals, such as sodium or potassium hydroxide. Furthermore, sulfuric acid is needed to neutralize the used caustic solutions. By contrast, simple tap water would be ideal for use with the wiping cylinder because of the environmental advantages due to reduction in use of

chemicals. However, the intaglio printing inks which are generally used in the industry do not disperse sufficiently in municipal water.

To print on a substrate using the intaglio printing process, after the engravings have been inked and the excess ink removed, the printing cylinder is pressed against the substrate using a very high compression of about 10,000 N per centimeter of the cylinder's length. Once the printed matter is dry (typically after several days of oxidative curing) it is desirable that it remains steadfast on the substrate and resistant to leakage or smudging on coming into contact with solvents or chemicals such as alkaline solutions.

Accordingly, it is highly desirable that the properties of an intaglio printing ink include both good dispersibility and good chemical/solvent resistance and, in particular, that such dispersibility include dispersibility in water.

It is known in the art of making of inks and coatings that dispersibility can be improved by using alkyds with high acid numbers but such components do not provide the desired dual properties of chemical resistance and water dispersibility.

In U.S. patent No. 4,764,215 it is claimed by Rudolph that drying oil soaps, prepared by high temperature saponification of unsaturated oils using metal hydroxides in the presence of triethanolamine, give inks with improved wipeability and resistance to water and eliminate volatile organic solvents. However, as disclosed in U.S. reissue patent No. 34,389 to Amon et. al., the ink compositions claimed by Rudolph are not satisfactory because they do not allow stable incorporation of even very low amounts of water, they do not sufficiently dry after printing and they are not resistant to the action of alkaline solutions.

It is also known in the art that the problems associated with an ink's lack of chemical resistance can be partly solved by the addition of components known to have high chemical resistance, such as dehydrated castor oil or epoxy esters of unsaturated fatty acids, but such additives usually result in significantly reduced dispersibility of the modified ink. Also, some such additives have poor solubility and require the use of a compatibilizing solvent, such as glycol ether. The addition of such low molecular weight compatibilizing materials (i.e. solvents) causes an increase in the total concentration of volatile organic solvents which introduces a

formulation problem because some jurisdictions, for environmental reasons, restrict the allowable concentration of such solvents in printing inks.

Therefore, there is a serious need in the printing industry for an intaglio printing ink having improved solvent and chemical resistance as well as improved dispersibility, including tap water dispersibility, while, at the same time, avoiding the use of high concentrations of volatile organic components.

SUMMARY OF THE INVENTION

In accordance with the invention there is provided an intaglio printing ink comprising an alkyd having an acid number in the range of 0 - 100, in the amount of 15 - 50 weight percentage, an unsaturated oily component in the amount of 5 - 15 weight percentage, an anionic or nonionic surfactant in the amount of 0.5 - 12 weight percentage and an organic base in the amount of 0.5 - 5 weight percentage and selected from the group consisting of alcohol-amines, cycloaliphatic amines and substituted polyethyleneimines, wherein the substituted polyethyleneimines are modified with epichlorohydrine or alkoxylated and the base has a boiling point higher than 150°C. The intaglio ink normally also comprises pigment in the amount of 0 - 15 weight percentage, an extender in the amount of 25 - 70 weight percentage and a wax compound in the amount of 0 - 15 weight percentage.

It is preferable that the surfactant have low molecular weight and that the molecular structure of the surfactant comprise bulky hydrophobic moieties.

The intaglio ink may also comprise water in an amount of 0 - 15 weight percentage.

Also, in accordance with a further embodiment of the invention there is provided an intaglio printing ink comprising a zwitterionic surfactant in the amount of 0.5 - 12 weight percentage and not separately including an organic base.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The intaglio printing inks of the present invention provide improved dispersibility and solvent/chemical resistance and can be formulated with relatively

low concentrations of volatile organic components. Further, the improved inks claimed herein are subject to being water washable unlike the inks which are now known and used in the industry.

The improved alkyd-based inks of the invention comprise a surfactant and an organic base. An unsaturated oily component as defined herein is also included either as a separate component or as part of the alkyd itself (i.e. residual oily components remaining in the alkyd and resulting from the process or manner of preparation of the alkyd). Also, commercial alkyd products sometimes have added within them, by the manufacturer, a separate unsaturated oily component, which adjusts the "oil length" of the alkyd. Proper oil length of the alkyd vehicle is required to achieve the optimum dispersibility of the ink formulations claimed herein.

The term unsaturated oily component used herein means glycerides of unsaturated fatty acids (mostly di- and triglycerides) or a mixture of unsaturated fatty acids (such as tung oil). The standard processes for the manufacturing of alkyds, such as alcoholysis or acidolysis followed by polycondensation with poly-carboxylic acids, usually, but not necessarily, result in an oil length which must be adjusted by means of the addition of an "oily component".

The term "oil length" herein is defined as the amount of oil (or fatty acid expressed as triglyceride) present as a percentage of the total non-volatile content (see, for example, the reference P. Oldring and G. Hayward, Resins for Surface Coatings, Vol. 1, page 143, 1987 edition by SITA Technology, London, England). Tung oil or bodied tung oil, although they are mixtures of unsaturated fatty acids, are here considered to be oily components because they increase the "oil length" of the formulation.

The surfactant may be an anionic or nonionic surfactant or a combination of these. Examples of suitable surfactants include, but are not limited to, the following:

(1) Ethoxylated alkylphenols, such as those sold under the trademarks Triton X-100, Triton X-165, Triton X-305, Tergitol NP-8, Tergitol NP-9, Tergitol NP-10 by Union Carbide Corporation of Danbury, Connecticut, U.S.A.

(2) Phosphate esters of ethoxylated phenol derivatives, such as phosphate ester of tristyrylphenol, available under the trademark Soprophor 3D33 from Rhodia/Rhone-Poulenc, Inc., Cranbury, New Jersey, U.S.A.

(3)Alkylbenzene sulfonic acids and their salts, such those sold under the trademarks Witconate 1260 and Witconate 60T, mixtures comprising salts of dodecylbenzenesulfonate from Witco Corp., Greenwich, Connecticut, U.S.A.

(4)Alkyl(sulfophenoxy)benzene sulfonic acids derivatives, such those sold under the trademarks Dowfax C6L, Dowfax C10L, Dowfax 3B0, Dowfax 2EP, Dowfax 2A0 and Dowfax 8390, salts or acid forms of alkyl(sulfophenoxy) benzenesulfonic acids from Dow Chemical Co., Midland, Michigan, U.S.A.

(5)Sulfonated Castor Oil, such as the product sold under the trademark FREEDOM SCO-70 by BF Goodrich Co., Charlotte, North Carolina, U.S.A.

(6)Diesters of succinic acid sulfonates, such as sodium dioctyl sulfosuccinate sold under the trademark Geropon SDS by Rhodia/Rhone-Poulenc, Inc., Cranbury, New Jersey, U.S.A.

(7) Ethoxylated sorbitan esters, such as ethoxylated sorbitan trioleate sold under the trademark Alkamuls PSTO-20 by Rhodia/Rhone-Poulenc, Inc., Cranbury, New Jersey, U.S.A.

(8) Phosphate esters of ethoxylated alcohols such as phosphate esters of ethoxylated tridecyl alcohol sold under the trademarks Rhodafac RS-710, Rhodafac RS-610 or Rhodafac RS-410, from Rhodia/Rhone-Poulenc, Inc., Cranbury, New Jersey, U.S.A.

Use of a zwitterionic surfactant produces a less successful result in that dispersiblilty in alkaline wiping solultions is not achieved but, nevertheless both dispersibility in tap water and good chemical resistance is achieved. The use of a zwitterionic surfactant also avoids the need to add an organic base because such a surfactant contains a base as part of its own molecular structure. That is, in the case of a zwitterionic surfactant the base and surfactant are combined in a single molecule.

Cationic surfactants are not suitable for use because they do not demonstrate an improvement in dispersibility for the resulting inks.

The organic base may be comprised of one or more organic base components, examples of which include, but are not limited to, the following:

(1)Ethanolamines, such as diethanolamine (DEA), triethanolamine (TEA), N-methyldiethanolamine (NMDEA), monomethylethanolamine (MMEA), 2-(2-aminoethoxy)ethanol (sold under the trademark DIGLYCOLAMINE agent), N,N-dimethyl-2-(2-aminoethoxy)ethanol (DMDGA) and tetramethyl bis(aminoethyl)ether, which are available from Huntsman Corp., Houston, Texas, U.S.A. (Some of these compounds are also available from Aldrich Co., Milwaukee, Wisconsin.)

(2)N-substituted morpholines, such as N-butylmorpholine (NBM)and the product sold under the trademark JEFFCAT DMDEE available from Huntsman Corp., Houston, Texas, U.S.A.

(3)Derivatives of polyethyleneimines, such as epichlorohydrin modified polyethyleneimine or 80 % ethoxylated polyethyleneimine available from Sigma-Aldrich Co., Milwaukee, Wisconsin, U.S.A.

(4)Polyoxyalkyleneamines, such as those sold under the trademarks JEFFAMINE D-230 and JEFFAMINE D-400 by Huntsman Corp., Houston, Texas, U.S.A.

The range of organic bases which are suitable for use in the invention are defined herein as organic amines selected from the group consisting of alcohol-amines, ring-containing nitrogen compounds and substituted polyethyleneimines, wherein the substituted polyethyleneimines are modified with epichlorohydrine or alkoxylated, and each of the organic amines of the group has a boiling point higher than 150°C.

The preferred concentration of the surfactant component of the ink is from 0.5 wt% to 12 wt% of the total ink, while the preferred concentration of the organic base is from 0.5 wt% to 5 wt% of the total ink. Most preferably, the concentration of the surfactant is from 2 wt% to 8 wt% and the concentration of the organic base is from 1 wt% to 4 wt% of the total ink. Although more than 5 wt% of organic base can be used, such an amount is usually detrimental to the chemical resistance of the print.

An intaglio printing ink comprised in accordance with the invention may comprise about 15-50 wt% alkyd having an acid number within the range of 0-100 (typically between 20 and 80), about 0.5-12 wt% surfactant and about 0.5-5 wt% organic base. Preferably, about 5-15 wt% of an unsaturated oily component (for example, linseed, soya, tung oil or bodied tung oil) is added. Also normally included in intaglio inks are pigment(s) which may be dry or flush and may include phtalocyanines and/or other organic and inorganic pigments, an extender such as barium sulfate or calcium carbonate, and a wax compound such as natural waxes (Carnauba, Candelilla etc.), or synthetic waxes (polyethylene, polytetrafluoroethylene, paraffin, etc.).

The preferred driers are compounds of cobalt, manganese, calcium and zinc. The ink composition may also comprise oxidatively curing epoxy esters, preferably having a high acid number, or alkyds modified with polyurethanes. In addition, the composition may include rheology modifiers, such as that sold under the trademark Bentone SD1 (available from Rheox, Heightstown, New Jersey, U.S.A.), or oligomers of ethylene oxide, propylene oxide or their combination, such as those sold under the trademarks Carbowax PEG 200 and Carbowax PEG 600 (available from Union Carbide, Danbury, Connecticut, U.S.A.). The function of such rheology modifiers is to adjust viscosity, yield point, tack and the printing behaviour of the resultant ink.

In addition to the above-specified surfactant, the ink composition may also include a surfactant having strong penetrating properties, such as sodium dioctyl sulfosuccinate (for example, that sold under the trademark Geropon SDS which is available from Rhodia, Cranbury, New Jersey, U.S.A.). Optionally, the ink composition also preferably includes an anti-blocking agent, such as that sold under the trademark Ceramid which is available from Lonza, Fair Lawn, New Jersey, U.S.A.

One preferred ink composition in accordance with the invention is the

following:

Component	Weight%
modified vehicle*	34.0
pigment	5.0
calcium carbonate	40.92
wax	9.0
drier (6% Mn)	0.29
drier (10% Ca)	0.29
surfactant**	7.0
base***	3.5

*the modified vehicle being comprised of 80 wt% of the commercial vehicle/varnish sold under the trademark Hydrokyd-9 by Lawter International of Northbrook, Illinois, U.S.A. and 20 wt% of bodied tung oil (being the selected unsaturated oily component).

**the surfactant being sold under the trademark Rhodafac RS-610 (see the above description for greater detail).

***the base being triethanolamine.

To prepare this composition the alkyd-based varnish and unsaturated oily component are mixed together. Then the pigment and the extender (i.e. calcium carbonate) are stirred into the mixture and the resulting mixture is ground on a three-roll mill until the desired level of pigment dispersion is achieved. Then the wax, driers and the surfactant and organic base additives are stirred into the mixture and the resulting mixture is passed through the three-roll mill. The resulting ink is then mixed to achieve uniform composition and packaged into containers.

The results of comparative test samples of 25 ink compositions, designated as ink samples P1-P25 herein, are provided below, at the end of this description, under Tables 1, 2, 3 and 4 for the purpose of illustrating the properties of dispersibility and solvent/chemical resistance achieved by the present invention.

The ink samples P1-P25 were prepared by mixing varnish (Hydrokyd-9) with bodied tung oil, and then stirring-in the pigment with the extender. This mixture was then mixed manually until all of the solids were completely wetted by

the varnish mixture. The wax compound was added to the resulting mixture and all large agglomerates were completely dispersed. Then the mixture was milled on a laboratory Muller (48 rotations) and the resulting ink samples were collected into closed vials for storage and testing. The specific formulation of each test sample is set out in Tables 1-4. In each case, 4 grams of the sample ink was prepared.

Table 1 illustrates the effect of different additives on the properties of ink. Table 2 illustrates the effect of using different organic bases on the ink properties and Table 3 illustrates the effect of using different surfactants, and water, on the ink properties. Table 4 illustrates the effect of using a zwitterionic surfactant (an amphoteric surfactant) on the ink properties.

The procedure used for the testing of the dispersibility of the ink samples was as follows. About 0.1 g of ink was collected on the end of a spatula and immersed in the tested solution (i.e. water or a caustic solution of specified concentration). The sample was kept still and separation of ink from the bulk of the sample was observed. The time from the start of immersion of the sample to the moment when a down-flowing streak of ink-water suspension was established was recorded as the dispersion time. As well, a qualitative evaluation of the amount of ink separated was made and the overall rating depended on both parameters.

The dispersibility ratings provided in the Tables are defined as follows:

E - time shorter than 5 seconds and large quantity of ink dispersion observed (excellent);

VG - time from 5 to 15 seconds and large quantity of ink dispersion observed (very good);

G - time from 15 to 30 seconds and large quantitY of ink dispersion observed (good);

M - time from 20 to 40 seconds and moderate quantity of ink dispersion observed (moderate);

P - time from 30 to 45 seconds and small quantity of ink dispersion observed (poor);

VP - time from 45 to 60 seconds and small quantity of ink dispersion observed (very poor);

ND - time longer than 60 seconds (not dispersing).

The property of solvent and chemical resistance of the test samples is rated on a scale from 0 to 10 according to the following:

0 - complete ink removal
1 & 2 - very poor resistance
3 & 4 - poor resistance
5 - just failed
6 - passed
7 & 8 - good resistance
9 & 10 - excellent resistance

The chemical resistance to alkaline solutions and to solvents was tested after storing the printed matter for seven days to allow for oxidative curing.

In Table 1 below ink sample P1, being a conventional alkyd-based intaglio ink without the addition of surfactant, organic base and drying tung oil, is shown to be non-dispersible in water or any alkaline solution having up to 1.5 wt% of NaOH. This ink sample also demonstrated very low alkaline and soap resistance. Ink sample P2 includes bodied tung oil over the conventional formulation of sample P1. The test results provided by sample P2 demonstrated only marginal improvement for alkaline resistance and no improvement for dispersibility. The test results for ink samples P3 and P4, which include organic base but not surfactant, show that the base alone or even in combination with bodied tung oil (as in sample P4) have no effect on dispersibility of the ink. However, ink sample P4 generally demonstrated higher chemical resistance than ink sample P3, indicating that the combination of bodied tung oil with an organic base produces a favourable effect on chemical resistance.

For ink sample P5 a surfactant (in the amount of 7.19 wt%) was added but without the addition of an organic base or drying oil and the results show no improvement for chemical resistance but some, limited improvement for dispersibility, in that the ink was shown to be dispersible in some alkaline solutions. Ink sample P6 comprised the combination of a surfactant with an organic base but without bodied tung oil and, as shown in Table 1, the results showed only limited improvement over the conventional ink formulation and the desired chemical

resistance was not gained, while water dispersibility was very limited. Similarly, for sample P7, comprising a combination of surfactant with bodied tung oil, but without an organic base, the test results show only a marginal, unsatisfactory level of improvement for the chemical resistance of the ink and an improvement in dispersibility.

The test results of ink sample P8, which includes each of the components - a surfactant, organic base and an unsaturated oily component (bodied tung oil), shows that proper combination of surfactant with a base (with optimized oil length) provides the desired results, namely, superior properties both in dispersibility and in chemical resistance. Solvent resistance, crumple resistance and rub resistance of the sample ink (P8) having the specified components are very good, as shown in Table 1.

Table 2 below illustrates the effect of various bases on the properties of the ink samples. The test results identify that the molecular structure of the base selected for use has a strong effect on the chemical resistance of the ink produced therefrom.

For example, ink sample P11, in which the organic base comprised an unsubstituted morpholine, did not provide an acceptable level of chemical resistance and the results produced by it were inferior to the results produced by ink sample P8 (see Table 1) in which triethanolamine was used. Similarly, in sample P10, the use of monoethanolamine did not achieve acceptable chemical resistance. However, in ink sample P9, the use of N-methyldiethanolamine produced good results. For ink samples P12, P13, P14 and P15, polyethyleneimine and derivatives thereof were used as the organic base and, as shown by Table 2, the results of the ink samples comprising an unsubstituted polyethyleneimine produced unacceptable results. However, the results of ink samples P12 and P15, comprising polyethyleneimine modified with epichlorohydrin and ethoxylated polyethyleneimine, respectively, showed acceptable chemical resistance and good dispersibility for the higher concentration alkaline solutions.

Table 3 below illustrates, on a comparison basis, the effect of using various surfactants on the properties of the inks. The test results indicate that ink samples P19, P22 and P23 (see Table 3)and P8 (see Table 1) provided the best results

with each of these showing both good chemical resistance and good dispersibility. The surfactants used for these ink samples, Rhodafac RS-610 and Soprophor 3D33, are low molecular weight surfactants and their molecular structures have bulky hydrophobic moieties which is a preferred characteristic for the surfactant to be selected for use in the formulations. The surfactant of ink samples P8 and P22, Rhodafac RS-610, is a phosphate ester of branched alcohol ethoxylate and, as such, it has a bulky hydrophobic part, and the surfactant of ink samples P19 and P23, Soprophor 3D33, is a phosphate ester of tristyrylphenol ethoxylate, which has an extremely bulky hydrophobic part. By contrast, the low molecular weight surfactant of sample P17, Triton X-100, which is an ethoxylate of octylphenol with an average number of ethylene oxide units equal to 9.5, does not have a bulky hydrophobic moiety and as such is not as effective in improving the desired properties of inks. The term "low molecular weight" with reference to the surfactant is used herein to mean surface active compounds with molecular weights below 5000 units of atomic mass.

The results of Table 3 also demonstrate the importance of the ionic form of the surfactant to be selected for use. Anionic surfactants (e.g. Rhodafac RS-610 and Soprophor 3D33) and nonionic surfactants (Triton X-100) were shown to be effective to improve the properties of the ink, but a cationic surfactant (e.g. Chemzoline T-11, alkyl aminoethyl imidazoline) was shown, by ink samples P20 and P21, to be completely ineffective for use as an agent to improve the dispersibility of the inks.

Table 3 also illustrates, by comparative sample inks P16 and P17 and inks P18 and P19, that the addition of an organic base (in these cases triethanolamine) resulted in improvements of both dispersibility and chemical resistance.

For ink samples P20 and P21, comprising a cationic surfactant, the test results demonstrated that they produced improved chemical resistance over the ink samples P1 and P2 but their dispersibility was unacceptable. In addition, since cationic surfactants are themselves bases, the addition of a base such as triethanolamine (see sample P21) provided only slight improvement in the chemical resistance of the sample.

The test results shown in Table 3 identify that still greater improvement in chemical resistance and in dispersibility may be achieved by adding about 4 wt.% of water to the ink composition. The sample inks P22 and P23 contained water accordingly, and demonstrated excellent water and alkaline dispersibility.

Table 4 below illustrates the effect of a zwitterionic surfactant, with and without the addition of an organic base, on the properties of the ink sample. As shown, the addition of this surfactant plus an organic base (triethanolamine) did not achieve the desired properties. This is because the zwitterionic surfactant, aminopropionate sold under the trademark Mirataine JC-HA, comprises an integral functional amino group and, therefore, the addition of a free base (triethanolamine), per ink sample P25, provided an excess of the amine functionality and resulted in lower chemical resistance.

However, the results of ink sample P24, which did not include the addition of a separate organic base component, show that the use of a zwitterionic surfactant provides significant success in that both dispersibility in tap water and good chemical resistance are achieved by using this surfactant. The test results for this ink sample further show that this ink did not provide acceptable dispersibility in alkaline solutions.

It will be appreciated by those skilled in the art that changes could be made to the specific examples of embodiments of the invention which are described herein without departing from the scope of the invention which has been made and is claimed by the applicants. It is to be understood, therefore, that the invention claimed by the applicants is defined by the appended claims and is not limited to any of the examples or modifications thereof which are described herein.

Table 1. Effects of additives on properties of inks

	Unmod. ink P1	Modif. ink P2	Modif. ink P3	Modif. ink P4	Modif. ink P5	Modif. ink P6	Modif. ink P7	Modif. ink P8
COMPOSITIONS, WT. %								
Vehicle Composition, wt. %								
Hydrokyd-9	100	80	100	80	100	100	80	80
Bodied tung oil	0	20	0	20	0	0	20	20
Ink Composition								
Vehicle	37.69	38.46	36.46	36.97	34.82	33.49	35.61	34.34
Magiesol 40	2.11	0	1.63	0	1.95	1.88	0	0
Pigment	5.26	5.38	5.08	5.17	4.86	4.68	4.99	4.81
Calcium carbonate	44.41	45.38	42.63	43.63	41.04	39.47	42.01	40.52
Wax	9.91	10.12	9.80	9.74	9.16	8.81	9.38	9.04
Mn drier, 6% active	0.31	0.33	0.29	0.31	0.29	0.28	0.30	0.29
Ca drier, 10% active	0.31	0.33	0.29	0.31	0.29	0.28	0.30	0.29
Accelerator Dri Rx-HF	0	0	0	0	0.4	0.49	0	0
Surf. (Rhodafac RS-610)	0	0	0	0	7.19	7.11	7.41	7.14
Base: triethanolamine	0	0	3.82	3.87	0	3.51	0	3.57
DISPERSIBILITY								
Tap water	ND	ND	ND	ND	ND	M	VP	VG
Low Concentration of NaOH								
0.125 % NaOH	ND	ND	ND	ND	VP	P	VP	G
0.25 % NaOH	ND	ND	ND	ND	G	G	E	E
0.5 % NaOH	ND	ND	ND	ND	VG	VG	E	E
High Conc. of NaOH								
1.0 % NaOH	ND	ND	ND	ND	M	G	VG	VG
1.5 % NaOH	ND	ND	ND	ND	M	M	G	G
CHEMICAL RESISTANCE								
(Tests on draw-downs)								
Alkaline Solutions								
2% NaOH, 30 min., 25 °C	1	2	1	8	1	1	3	8
1% Na_2CO_3, 0.5% Persil, aq., 30 min., 80 °C	1	1	1	6	0	0	1	8
(Tests on printed proofs)								
Acids and Bases								
Hydrochloric Acid, 5%, 30 min., RT	8	8	7	8	7	8	7	8
2 % Sulfuric acid, 30 min., RT	7	8	7	8	7	8	7	8
Acetic Acid, 20%, 30 min., RT	7	8	6	8	7	7	7	8
NaOH, 2%, 30 min., RT	0	5	1	7	0	0	6	7
Bleach (Na hyp.), 5%, 30 min., RT	7	7	8	8	8	7	8	7
1% Na_2CO_3, 0.5% Persil, 30 min., 80 °C	1	4	1	7	1	1	7	8
Solvents / Laundry								
Ethanol, 30 min., RT	7	8	8	8	8	7	8	8
Ethyl Acetate, 30 min., RT	7	8	8	8	8	8	8	8
Trichloroethylene, 30 min., RT	8	8	7	8	8	8	8	8
Xylene, 30 min., RT	7	8	8	8	8	8	8	8
Solvent Naptha, 30 min., RT	7	7	7	8	8	8	8	8
Perchloroethylene, 30 min., RT	8	7	7	7	7	8	7	8
Acetone, 5 min.,	8	8	8	8	7	8	8	7
Synthetic perspiration, 10 min., 40 °C	7	8	8	7	8	8	8	8
Sunlight soap, 10%, 30 min., 80 °C	4	4	3	8	3	3	7	7
Laundry test	8	9	8	9	7	9	9	9
Physical Resistance Tests								
IGT crumple test, 8 crumples		9	9	9	9	9	9	99
Rub test, 200 cycles	9	9	9	9	9	9	9	9

Table 2. Effects of various bases on properties of inks.

	Ink P9	Ink P10	Ink P11	Ink P12	Ink P13	Ink P14	Ink P15
COMPOSITIONS, WT.%							
Vehicle Composition. wt.%							
Hydrokyd-9	80	80	80	80	80	80	80
Bodied tung oil	20	20	20	20	20	20	20
Ink Composition							
Vehicle	34.48	34.55	34.45	34.49	34.46	34.43	34.10
Pigment	4.75	4.76	4.74	4.75	4.75	4.74	4.76
Calcium carbonate	40.35	40.44	40.33	40.37	40.34	40.29	40.15
Wax	9.16	9.18	9.15	9.16	9.15	9.14	9.12
Mn.drier, 6% active	0.30	0.30	0.31	0.29	0.30	0.30	0.30
Ca drier, 6 % active	0.30	0.30	0.31	0.31	0.30	0.31	0.30
Accelerator, Dri RX-HF	0.03	0.03	0.03	0.03	0.03	0.03	0.37
Surf. (Rhodafac RS-610)	7.08	6.96	7.12	7.07	7.07	7.17	7.16
Organic base	3.55	3.48	3.57	3.53	3.60	3.59	3.74
Organic base formula	NMDEA	MEA	Morph.	PEI epi.	PEI linear	PEI mol. wt. 600	PEI/ EO
DISPERSIBILITY							
Tap water	VG	VG	E	VP	VP	ND	VP
Low Concentration of NaOH							
0.125 % NaOH	G	G	VG	ND	ND	ND	ND
0.25 % NaOH	G	G	G	ND	M	VP	ND
0.5 % NaOH	G	G	G	G	E	E	E
High Concentration of NaOH							
1.0 % NaOH	G	G	VG	G	VG	VG	G
1.5 % NaOH	G	G	G	G	VG	G	G
CHEMICAL RESISTANCE (Tests on draw-downs)							
Alkaline Solutions							
2% NaOH, 30 min., 25 °C	8	4	1	7	3	4	7
1% Na_2CO_3, 0.5% Persil, aq., 30 min., 80 °C	6	3	2	6	2	4	6

NMDEA - N-methyldiethanolamine; (Aldrich Co., Milwaukee, WI)
MEA - Monoethanolamine; (Aldrich Co., Milwaukee, WI)
Morph. - Morpholine; (Aldrich Co., Milwaukee, WI)
PEI epi. - Polyethyleneimine modified with epichlorohydrin, 17 % aq. solution, molecular wt. 20,000; (Aldrich Co., Milwaukee, WI)
PEI linear - Linear polyethyleneimine, aver. mol.wt. 423 ; (Aldrich Co., Milwaukee, WI)
PEI low m. wt. - Polyethyleneimine, mol. wt. 600, branched structure; (Aldrich Co., Milwaukee, WI)
PEI / EO - Polyethyleneimine, 80 % ethoxylated, 37 % aq. solution, mol. wt. 50,000; (Aldrich Co., Milwaukee, WI)

Composition of pigments: Carmine Red: 88.88 wt.%, Phtalocyanine Blue: 7.54 wt.%, Carbon Black: 3.58 wt.%. Wax: 67 wt.% Carnauba wax compound, 33 wt.% Candelilla wax compound.

Table 3. Effects of various surfactants and water on properties of inks.

	Ink P16	Ink P17	Ink P18	Ink P19	Ink P20	Ink P21	Ink P22	Ink P23
COMPOSITIONS, WT. %								
Vehicle Composition, wt. %								
Hydrokyd-9	80	80	80	80	80	80	80	80
Bodied tung oil	20	20	20	20	20	20	20	20
Ink Composition								
Vehicle	35.41	34.24	35.61	34.34	35.64	34.34	32.83	32.86
Pigment	5.00	4.84	4.99	4.81	4.98	4.80	4.59	4.60
Calcium carbonate	41.65	40.26	42.02	40.52	41.96	40.43	38.66	38.69
Wax	9.29	8.98	9.37	9.04	9.53	9.18	8.78	8.78
6% Mn drier	0.30	0.29	0.30	0.29	0.31	0.30	0.29	0.29
10% Ca drier	0.30	0.29	0.30	0.29	0.31	0.30	0.29	0.29
Accelerator Dri Rx-HF	0.73	0.69	0	0	0	0	0	0
Surfactant conc.	7.32	6.94	7.41	7.14	7.27	7.00	6.76	6.68
Surfactant name	Trit.-X	Trit.-X	Sopr.	Sopr.	T-11	T-11	RS-610	Sopr.
Water	0	0	0	0	0	0	4.26	4.42
Base: triethanolamine	0	3.47	0	3.57	0	3.65	3.54	3.39
DISPERSIBILITY								
Tap water	G	VG	M	G	ND	ND	E	E
Low Concentration of NaOH								
0.125 % NaOH	G	G	ND	M	ND	ND	M	M
0.25 % NaOH	VG	E	G	VG	ND	ND	G	G
0.5 % NaOH	VG	VG	VG	VG	ND	ND	E	E
High Conc. of NaOH								
1.0 % NaOH	G	G	G	G	ND	ND	VG	VG
1.5 % NaOH	M	P	M	M	ND	ND	G	G
CHEMICAL RESISTANCE								
(Tests on draw-downs)								
Alkaline Solutions								
2% NaOH, 30 min., 25 °C	1	7	8	8	7	8	10	10
1% Na_2CO_3, 0.5% Persil, aq., 30 min., 80 °C	1	5	3	9	2	3	10	10

Trit.-X - Triton-X 100 nonionic surfactant (Union Carbide, Danbury, CT)
Sopr. - Soprophor 3D33, anionic surfactant (Rhodia, Cranbury, NJ)
T-11 - Chemzoline T-11, cationic surfactant (Chemron Corp., Paso Robles, CA),
RS-610 - Rhodafac RS-610, anionic surfactant (Rhodia, Cranbury, NJ)

Table 4. Effects of amphoteric surfactant on properties of inks.

	Ink P24	Ink P25
COMPOSITIONS, WT. %		
Vehicle Composition, wt. %		
Hydrokyd-9	80	80
Bodied tung oil	20	20
Ink Composition		
Vehicle	35.72	34.41
Pigment	4.90	4.72
Calcium carbonate	41.83	40.29
Wax	9.45	9.10
Mn drier, 6 % active	0.28	0.27
Ca drier, 10% active	0.35	0.34
Accelerator Dri Rx-HF	0.00	0.00
Surfactant conc.	7.47	7.31
Surfactant name	Mirat. JC-HA	Mirat. JC-HA
Base: triethanolamine	0	3.56
DISPERSIBILITY		
Tap water	M	M
Low Concentration of NaOH		
0.125 % NaOH	P	VP
0.25 % NaOH	VP	VP
0.5 % NaOH	VP	ND
High Conc. of NaOH		
1.0 % NaOH	VP	ND
1.5 % NaOH	VP	ND
CHEMICAL RESISTANCE		
Alkaline Solutions		
2% NaOH, 30 min., 25 °C	8	6
1% Na_2CO_3, 0.5% Persil, aq., 30 min., 80 °C	7	4

Mirat. JC-HA - Mirataine JC-HA, aminopropionate, amphoteric surfactant, (Rhodia, Cranbury, NJ)

WHAT IS CLAIMED IS:

1. An intaglio printing ink comprising:

(a) an alkyd having an acid number in the range of 0 - 100, in the amount of 15 - 50 weight percentage;

(b) an anionic or nonionic surfactant in the amount of 0.5 - 12 weight percentage; and,

(c) an organic base selected from the group consisting of alcohol-amines, ring-containing nitrogen compounds and substituted polyethyleneimines, wherein said substituted polyethyleneimines are modified with epichlorohydrine or alkoxylated and said base has a boiling point higher than 150°C, in the amount of 0.5 - 5 weight percentage.

2. An intaglio printing ink according to claim 1, further comprising an unsaturated oily component in the amount of 5 - 15 weight percentage.

3. An intaglio ink according to claim 2, further comprising pigment in the amount of 0 - 15 weight percentage, an extender in the amount of 25 - 70 weight percentage and wax compound in the amount of 0 - 15 weight percentage.

4. An intaglio ink according to claim 1 wherein said surfactant has low molecular weight.

5. An intaglio ink according to claim 2 wherein said surfactant has low molecular weight.

6. An intaglio ink according to claim 3 wherein said surfactant has low molecular wight.

7. An intaglio ink according to claim 2 wherein the molecular structure of said surfactant comprises bulky hydrophobic moieties.

8, An intaglio ink according to claim 3 wherein the molecular structure of said surfactant comprises bulky hydrophobic moieties.

9. An intaglio ink according to claim 4, further comprising water in an amount of 0 - 15 weight percentage.

10. An intaglio ink according to claim 5 and further comprising water in an amount of 0 - 15 weight percentage.

11. An intaglio printing ink comprising:

(a) an alkyd having an acid number in the range of 0 -100, in the amount of 15 - 50 weight percentage; and,

(b) a zwitterionic surfactant in the amount of 0.5 - 12 weight percentage.

12. An intaglio ink according to claim 11, further comprising an unsaturated oily component in the amount of 5 - 15 weight percentage.

13. An intaglio ink according to claim 12 further including pigment in the amount of 0 - 15 weight percentage, an extender in the amount of 25 - 70 weight percentage and wax compound in the amount of 0 - 15 weight percentage.

14. An intaglio ink according to claim 13 and further comprising water in an amount of 0 - 15 weight percentage.

INTERNATIONAL SEARCH REPORT

Int. ional Application No
PCT/CA 00/01462

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 569 701 A (MOYNIHAN JOHN T) 29 October 1996 (1996-10-29) column 1, line 48 -column 2, line 46 column 2, line 47-57 column 6, line 66 -column 7, line 2 column 7, line 17-27 column 7, line 28-52 column 7, line 53-57	1-14
A	US 3 342 764 A (ARLEEN S. VARRON) 19 September 1967 (1967-09-19) examples I-VIII,XII	1-3, 11-13
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☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 March 2001	15/03/2001

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/CA 00/01462

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