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(54) Title: IMPROVEMENTS IN OR RELATING TO GRAVURE PRINTING INKS

(57) Abstract: Mixed paraffinic/naphthenic fluids boiling in the range of 80 °C to 140 °C are used as solvents for gravure printing inks; the solvents are effective substitutes for toluene and may be readily recovered and recycled using conventional techniques.

IMPROVEMENTS IN OR RELATING TO GRAVURE PRINTING INKS

The present invention relates to improvements in or relating to gravure printing inks.

Various methods are used for printing. The method that is used depends upon the nature of the materials to be printed, the quality and nature of the substrate that is to be printed upon and the required quality of the printing. Widely used printing methods include letterpress, flexography, gravure and offset. Offset printing is used for newspapers, magazines, books, brochures, poster and cards. Gravure printing is used for many packaging applications, large circulation magazines and pressure sensitive labels. Letterpress printing tends to be used for local newspapers, labels and packaging. Flexography printing is used for packaging, newspapers and wall covering.

In offset printing an image is transferred from a printing plate provided with ink to a blanket roller and the image is then transferred from the blanket roller to the substrate. Offset printing is frequently used for the printing of newspaper. In gravure printing, sometimes known as rotogravure, the image to be printed is etched into a printing plate or roller. Ink is provided directly to the plate or roller and is then transferred to the substrate by bringing the substrate into contact with the surface of the plate or roller. Gravure printing is often used for very long production runs. It will be appreciated that whatever printing technique is employed, the activities are performed at high speed.

The requirements of an ink for use in the different printing techniques are totally different. For example in offset printing the ink needs to be of high viscosity and paste-like so that it is retained by the plate or roller. For gravure inks however, a low viscosity, mobile product is required to enable the ink to readily enter the engraved elements of the printing plate and to ensure that it can be rapidly taken up by the paper due to capillary action. The present invention is concerned with gravure printing inks and in particular with solvents that are used in gravure inks.

In gravure printing the printing surface is typically a rotating cylinder, frequently a copper cylinder, which rotates in a bath of the ink to pick up the ink in the engraved elements of the cylinder. Excess ink is removed from the roller by a blade and the roller then comes into contact with the substrate to be printed, typically paper or plastic. The image is thereby transferred to the substrate, which then passes into an oven where the ink solvent is vaporised so that the ink is dried and a secure print image remains on the substrate. The solvent is then recovered and recycled. A typical gravure ink consists of a solvent, a binder resin, a pigment and optionally other additives. Typically the ink comprises from 40% to 60% by weight of solvent, based on the total weight of the ink formulation. The inks are typically provided to the printer (operator) in concentrated form known as an ink concentrate. This is then diluted with additional solvent, perhaps containing other additives, which may be based on solvent that is recycled at the print works. Fresh solvent may also be required to make up for solvent that is lost during solvent recovery. Accordingly the present invention is concerned with fluids that are used as solvents for gravure ink concentrates, recycle solvents and make up solvents useful in gravure inks.

The typical requirements of a gravure ink are as follows: good dispersion, which can be achieved by various manufacturing techniques (e.g. use of chips and pre-dispersed pigments, conventional dispersion equipment like bead mills, rod mills, ball mills); good strength, assessed by use of drawdown technique and by 'bleaching'; and transparency and gloss, which depend upon the nature of the substrate. For publications, a glossy transparent ink will appear weak on paper, in comparison with a matt opaque ink. The gloss can be measured by a gloss meter. The ink must dry quickly and the ink-maker will normally use the Hegmann Gauge to compare the drying rate of a test ink against that of a known standard.

In gravure printing, the ink formulator is generally solely concerned with the tack of the dried ink, especially in areas of two or more colour superimposition. The basic principle of a tackmeter is that two rollers, one of which is driven, rotate with a film of ink of known thickness over them. The second roller may be

supported in a manner which permits the measurement of the force required to hold it in a stationary position relative to the driven roller.

A typical gravure ink concentrate formulation comprises in weight % based on the total weight of the concentrate:

Pigment (or dyestuff)	4-12%
Extender pigment	0-8%
Resin	10-30%
Solvent	40-60%
Other additives*	2-10%

(* which may include plasticizer and wax)

A typical ink formulation (after dilution of the concentrate with fresh and/or recycle solvent) for use on the printing press comprises in weight % based on the total weight of the formulation:

Pigment (or dyestuff)	4-6%
Extender pigment	0-4%
Resin	9-15%
Solvent	70-85%
Other additives *	2-5%

(* which may include plasticizer and wax)

Gravure inks dry by the evaporation of the solvent and normally there is no oxidation or chemical change once the ink film is dry. Printing at higher speeds demands faster drying speed and hence lower viscosities, to enable the ink to flow rapidly out of the cells of the print plate or roller at the point of impression on the substrate.

It will therefore be appreciated that gravure printing requires the use and handling of considerable volumes of solvent. Properties of the solvent that are important for gravure printing, in addition to a low viscosity, are that it has good solvency power for the resins, pigments and other additives that are used in the ink. In

addition the solvent must have a volatility that enables rapid drying of the ink on the substrate and ready recovery of the solvent. However, the volatility should not be such that the ink may dry on the engraved printing plate as this can block some of the engraved elements.

In solvent recovery the printed substrate is heated to dry the inks on the substrate. The solvent is evaporated and the vapours are adsorbed on an adsorbent such as carton, eg activated carbon, and then desorbed with steam. The desorbed material is then recovered by condensation and dried for reuse.

Toluene has been widely used as a solvent for gravure printing inks. Toluene has a desirable combination of properties for this use. It has a good solvency power, a boiling point of 111°C, a flash point of 4°C and is readily recoverable by the techniques discussed above. However, although toluene is an effective solvent, its use raises environmental and health concerns. Accordingly there is a need for alternative solvents for gravure printing. The need for an alternative solvent has been recognised in, for example, Japanese patent publications 2001-240787 and 2003-003104 which propose that various derivatives of cyclohexane be used. Japanese Patent Publication 2003-003104 uses methyl cyclohexane, ethyl cyclohexane, dimethyl cyclohexane or propyl cyclohexane or mixtures thereof.

Hydrocarbon fluids useful as solvents are usually obtained from refinery streams, typically derived from crude oil. Where toluene has been used it has been obtained by reforming naphtha and then separation by distillation to obtain the toluene. Reforming is, however, an expensive process. If methyl cyclohexane, ethyl cyclohexane or other cyclohexyl derivatives are required it is necessary to hydrogenate the aromatic compounds that are obtained by reforming the naphtha. Hydrogenation of pure compounds such as toluene, xylene or ethyl benzene is a further expensive step in the production of the gravure ink solvents proposed in Japanese Patent Publications 2001-240787 and 2003-003104.

The present invention aims to provide an alternative aliphatic solvent for gravure printing inks which can be produced by a simpler process than the 100% naphthenic solvents that are proposed in Japanese Patent Publications 2001-240798 and 2003-003704. The use of the solvents provided by the present invention also has additional benefits when compared with the use of toluene, in that they have a lower density than toluene and hence larger solvent volumes can be obtained for a given weight of material.

The present invention therefore provides the use as a solvent for gravure inks of an aliphatic fluid boiling in the range of from 80°C to 140°C and comprising from 45% to 70% paraffinic molecules and from 30% to 55% naphthenic molecules the combined weight of paraffinic molecules and naphthenic molecules being at least 90% of the total fluid weight, preferably at least 95%.

The boiling points and boiling ranges specified herein are as measured according to ASTM D 86.

It is preferred that the fluids used as solvents in the present invention are completely free of aromatic molecules. However, small amounts can be tolerated and still achieve the benefits the invention. For example, toluene could be present up to about 10 wt %, although preferably less than 1% and if present more preferably from 100-1000 ppm. Benzene should preferably not be present in an amount greater than 0.1 wt %. It is also preferred that the fluids contain from 45 to 60% paraffinic molecules and 40 to 55% naphthenic molecules. Preferably the total of paraffinic and naphthenic molecules in the fluid is from 95% to 100%, more preferably greater than 95%, and most preferably 100% of the fluid.

The invention further provides the use as a solvent for gravure inks of an aliphatic fluid boiling in the range 80 to 140°C, which fluid comprises a mixture of paraffinic and naphthenic molecules, contains no more than 10% aromatic molecules and is derived from crude oil by distillation followed by hydrogenation and fractionation.

It is preferred that the fluids have a narrow boiling range, preferably having initial to final boiling points that differ by no more than 40 degrees C, more preferably not more than 30 degrees C, most preferably not more than 20 degrees C. Preferred fluids boil in the range 80°C to 120°C or in the range 100°C to 140°C, more preferably in the range 100°C to 120°C, although fluids boiling in the range 120°C to 140°C can be used.

The fluids that are preferably used are those where the molecules fall in the C_6 to C_9 carbon range, ideally with no or only minimal components falling outside that carbon number range. Most preferably the carbon numbers of the various components of the fluids are predominantly in the C_7 to C_8 range. For example, 50% or more, more preferably at least 80% of the components are C_7 or C_8 compounds.

The fluids used as solvents in the present invention have good solvency power for gravure printing ink formulations. Furthermore we have found that they may be readily recovered employing the techniques traditionally used for the recovery of toluene solvent from gravure inks. Accordingly the fluids can be substituted for toluene as solvent in such processes without requiring significant modifications of existing printing facilities.

The chemical nature and composition of hydrocarbon fluids vary considerably. They contain paraffinic and naphthenic molecules, where paraffinic means non cyclic aliphatic and naphthenic means cyclic aliphatic. Important properties of hydrocarbon fluids are the distillation range generally determined by ASTM D 86, flash point, density, Aniline Point (which is most often used to provide an estimate of the solvency power of mixtures) as determined by ASTM D 611, aromatic content, viscosity, colour and refractive index. We prefer that the fluids have narrow boiling point ranges as indicated by a narrow range between Initial Boiling Point (IBP) and Final Boiling Point (FBP) according to ASTM D 86; the use of the narrow cuts provides the benefit of a precise flash point which is important for safety reasons. The narrow cut also brings important fluid

properties such as a better defined viscosity, improved viscosity stability and defined evaporation conditions, better defined surface tension, aniline point or solvency power. Further requirements for the fluids are that they have good cold flow properties so that their freezing points are as low as possible such as to enable outdoor storage. Preferably the fluids used as solvents in accordance with the present invention have an aniline point from 55°C to 65°C.

Hydrocarbon fluids are typically derived by refining refinery streams in which the fluid having the desired properties is obtained by subjecting the most appropriate feed stream to distillation, fractionation and purification. The purification typically consists of hydrodesulphurisation and/or hydrogenation to reduce the sulphur content or, in some instances, to eliminate the presence of sulphur and to reduce or eliminate aromatics and unsaturates. Traditionally, aliphatic hydrocarbon fluids are produced from the products of atmospheric distillation such as virgin or hydro-skimmed refinery petroleum cuts which are deeply hydrodesulphurised and fractionated. The product that has been deeply hydrodesulphurised and fractionated may be hydrogenated to saturate any aromatics that are present. Hydrogenation can also occur prior to the final fractionation.

Typically in a refinery the crude oil is first subject to atmospheric distillation to obtain the useful light products. The solvents that are used in the present invention may be obtained from the products of atmospheric distillation. The residue from the atmospheric distillation is then subject to vacuum distillation to take off the vacuum gas oil cut. The vacuum gas oil cut from the vacuum distillation may then be subjected to cracking to produce upgrade materials from which the solvents used in this invention can be obtained. Hydrocracking is a technique that is frequently used to upgrade vacuum gas oil.

Hydrocarbon fluids have high purity requirements; generally sulphur levels below 10 wt. ppm, preferably below 5 wt ppm and frequently less than 1 wt ppm. These very low levels of sulphur are measured by ASTM D 4045. The fluids also need

to satisfy tight ASTM D 86 distillation characteristics which is the preferred test method for the fluids used according to the present invention. These fluids are typically obtained from one of the side streams of atmospheric distillation. However, the sulphur and aromatics content of these side streams, especially from the second or third side streams, tend to be high and these increase as the final boiling point of the stream increases. Accordingly it may be necessary to hydrodesulphurise these side streams from atmospheric distillation to remove the sulphur and hydrogenate the streams to remove the aromatics. In practice, this places an upper limit of about 320°C on the final boiling point of the stream that can be used prior to fractionation because the heavy, higher boiling molecules are more difficult to desulphurise and need to be hydrofined at a higher temperature.

The fluid systems used as solvents for gravure inks in accordance with the present invention can be a mixture of a large number of aliphatic compounds, preferably those in the C_6 to C_9 carbon number range and more preferably predominantly in the C_7 and C_8 carbon number range. Previous commercial gravure ink solvent systems have been based on pure compounds (such as toluene) or mixtures of a few (two or three) pure compounds such as in Japanese Patent Publications 2001-240787 and 2003-003104. This has had the advantage that the material that is recovered in the traditional solvent recovery processes is identical to the starting solvent and the material can be recycled several times whilst retaining the properties that make the material desirable for use as solvent for gravure printing inks. We have surprisingly found that the composition of the fluids used according to the present invention remains substantially unchanged during recycle. We have found that although there may be a minimal change during initial recycles, the change is significantly reduced in subsequent recycles. Accordingly, when using the fluid system as solvent according to the present invention, the properties of the fluid that make it desirable for use as a gravure ink solvent are retained during several recycles of the fluid. This advantageous feature can be optimised by judicious selection of the adsorbent employed in the recovery stage.

Solvent recovery in gravure printing is generally initiated in the oven (typically by a forced air stream maintained at a temperature of from 40°C to 60°C) through which the printed substrate passes and where the ink is dried on the substrate eg paper. The solvent fluid vaporises and passes out of the oven into a bed of carbon, which may be activated carbon, where the residual solvent fluid is adsorbed from the stream onto the carbon. Subsequently the solvent fluid is removed from the carbon by steaming under pressure, typically with steam at for example 130°C to 140°C; the fluid is then condensed from the gaseous stream, separated from water, dried and is then ready for reuse as a solvent for the ink concentrate.

The following table provides the initial composition (in wt %) (as determined by gas chromatography [GC]) of a fluid as specified for use as a gravure ink solvent according to the present invention. The table also provides the composition after each of five laboratory scale recovery cycles employing activated carbon adsorption. In the table, the designations T, C describe the isomeric structure of the molecule. For example 1.T2, C4, Tri-methyl-cyclo-pentane designates that the methyl group on ring position 2 is trans to the methyl group at position 1; and the methyl group at ring position 4 is cis to the methyl group at position 1.

	Original Composition	1st	2nd	3rd	4th	5th
Components		Recovery	Recovery	Recovery	Recovery	Recovery
2-Me-pentane						
3-Me-pentane	0.01					
n-hexane	0.28	0.37	0.31	0.29	0.28	0.27
Me-Cyclo-pentane	0.35	0.50	0.42	0.39	0.36	0.34
2,4 di-Me-pentane	0.05	0.05	0.05	0.05	0.05	0.05
2,2,3 tri-Me-butane						
3,3-di-Me-pentane	0.02	0.01	0.01	0.01	0.01	0.01
Cyclohexane	0.70	0.91	0.77	0.73	0.69	0.65
2 Methyl-hexane	1.02	1.05	1.04	1.02	1.01	1.01
2.3 Di-methyl-pentane	0.54	0.56	0.54	0.53	0.53	0.52
3 Methyl-hexane	2.03	2.04	2.03	2.00	1.99	1.98
1.C3,Di-methyl-cyclo-pentane	0.64	0.65	0.62	0.61	0.61	0.60
1.T3,Di-methyl-cyclo-pentane	0.66	0.67	0.65	0.60	0.64	0.64
3 Ethyl-pentane	0.25	0.25	0.24	0.28	0.23	0.22
1.T2,Di-methyl-cyclo-pentane	1.83	1.83	1.76	1.74	1.73	1.72
n-Heptane	14.09	14.30	14.50	14.48	14.41	14.38
1.C2,Di-methyl-cyclo-pentane	0.67	0.66	0.64	0.64	0.64	0.64
Methyl-cyclo-hexane	23.46	22.34	21.78	21.64	21.80	21.64
2.4 Di-methyl-hexane	1.31	1.30	1.35	1.35	1.34	1.35
Ethyl-cyclo-pentane	5.26	5.15	5.16	5.17	5.19	5.19
1.T2,C4,Tri-methyl-cyclo-pentane	2.40	2.22	2.23	2.23	2.24	2.25
1.T2,C3,Tri-methyl-cyclo-pentane	2.94	2.88	2.87	2.89	2.89	2.90
2.3.4 Tri-methyl-pentane	0.39	0.37	0.38	0.38	0.38	0.38
2.3 Di-methyl-hexane	1.15	1.15	1.17	1.18	1.19	1.18
2 Methyl,3 ethyl-pentane	1.28	0.77	0.79	0.80	0.78	0.80
1,1,2-tri-Me-Cyclo-pentane						
2 Methyl-heptane	7.82	8.12	8.38	8.46	8.41	8.50
4 Methyl-heptane	2.29	2.37	2.44	2.47	2.45	2.48
3.4 Di-methyl-hexane	0.57	0.57	0.58	0.59	0.58	0.59
3 Methyl-heptane	5.40	5.35	5.50	5.55	5.52	5.59
sum:1.C3 Di-methyl-cyclo-hexane	0.00					
1.T4 Di-methyl-cyclo-hexane	5.30	5.00	4.96	4.96	4.97	5.00
sum:1.1 Di-methyl-cyclo-hexane	0.00					
1 Methyl,T3 ethyl-cyclo-pentane	0.48	0.42	0.40	0.38	0.37	0.36
sum:1 Methyl T2 ethyl-cyclo-pentane	1.00	1.02	1.04	1.06	1.08	1.10
1 Methyl C3 ethyl-cyclo-pentane	2.80	2.78	2.76	2.78	2.78	2.81
n-Octane	7.24	7.56	7.78	7.91	7.82	7.94
C8 cyclic	1.46	1.60	1.58	1.58	1.59	1.59
2.3.5 Tri-methyl-hexane	0.97	0.94	0.93	0.93	0.93	0.94
2.2 Di-methyl-heptane	0.19	0.18	0.20	0.20	0.20	0.20
sum:2.4 Di-methyl-heptane	0.00	0.05	0.07	0.06	0.07	0.07
2 Methyl-4ethyl-hexane	0.20	0.15	0.16	0.16	0.17	0.16
2.6 Di-methyl-heptane	0.09	0.12	0.15	0.15	0.15	0.15
2.5 Di-methyl-heptane	0.23					
4.4 Di-methyl-heptane	0.17	0.45	0.46	0.46	0.48	0.47
3.3 Di-methyl-heptane	0.80	0.83	0.83	0.82	0.85	0.84
C8 's	1.62	2.20	2.18	2.21	2.20	2.21

2,3,3 Tri-methyl-hexane	0.07	0.09	0.12	0.10	0.13	0.11
C9 's	0.11	0.15	0.18	0.14	0.24	0.15
Total	100.03	99.98	100.01	99.98	99.98	99.98

The solvent boils in the range 100 to 120°C.

The results indicate that the fluid is advantageously usable as a solvent system according to the present invention. It has a recycle potential comparable to that of toluene and can therefore be substituted for toluene in existing gravure printing facilities with little or no need to modify the equipment used for recovery and recycle of the solvent.

According to a further aspect of the invention there is provided a gravure ink concentrate comprising in weight %, based on the total weight of the concentrate:

pigment or dyestuff	4–12%
extender pigment	0–8%
resin	10–30%
fluid	40–60%
plasticizer, and wax	2–10%

where the fluid is an aliphatic hydrocarbon fluid as hereinbefore described with reference to the mentioned use as a solvent in gravure printing inks.

According to yet another aspect of the invention there is provided a gravure printing ink comprising in weight % based on the total weight of the ink :

pigment or dyestuff	4–6%
extender pigment	0–4%
resin	9–15%
fluid	70–85%
other additives optionally including plasticizer and wax	2–5%

where the fluid is an aliphatic hydrocarbon fluid as hereinbefore described with reference to the mentioned use as a solvent in gravure printing inks.

The ink may acquire the above formulation after dilution with fresh and/or recycle solvent for use on the printing press.

The components of gravure inks and concentrates according to the invention are discussed hereinafter.

Typical resins that are used in gravure inks are film-forming, hard, amorphous, low- odour, usually colourless or pale or transparent, and should be soluble in the solvent fluid. The resin assists the wetting of the pigment to ensure good pigment dispersion and stability. The viscosity of the varnish prepared by dissolving the resin in the solvent fluid should increase as the resin solids increase, and a thin film of varnish when exposed to air and heat should release its solvent quickly to give a tack-free homogeneous resin film. The resin also must impart adhesion of the ink to the substrate to be printed. When printing onto paper substrates, resins can be chosen to given penetration into the substrate and thus a low gloss level, or less penetration giving higher gloss levels.

The melting ranges of resins vary considerably and in many instances, softening point is less critical than adhesion, rub resistance or lightfastness. Resins should preferably not interact with the other constituents of the ink since otherwise gelation usually occurs. The major classes of resin that are used in practice are cellulose resins, polyamides, acrylics, vinyls and hydrocarbon-soluble resins. The major application for such resins is in the publication gravure field. Calcium and zinc calcium rosinates are soluble in both aromatic and aliphatic hydrocarbons giving high solids but low viscosity varnishes with excellent solvent release. In addition their low cost makes them an attractive proposition for publication gravure inks. However, they do suffer from the drawback of forming powdery films which tend to give poor rub resistance.

Hydrocarbon resins, while giving high solids, low viscosity varnishes, are generally inferior to rosinates with regard to solvent release.

Modified resins consist of a wide variety of chemical types of resin and can be used to modify the main vehicle system usually as a means to increase gloss or reduce cost. Typical of resins in this category are rosin modified maleics which can be produced with or without acidic functionality to vary the solubility. Typical uses of such resins are in combination with nitrocellulose or chlorinated rubber (generally low acid value grades), and since flexibility on film and foil is limited the main application is on paper and board. The resins have a typical rosin odour, which may be a disadvantage when the printing is in food packaging applications.

Ketone, aldehyde and styrene-allyl alcohol resins can be used to promote gloss improvement of nitrocellulose inks. Again, all suffer limited flexibility on film and especially on foil, and will generally detract from the heat resistance and solvent release of a nitrocellulose ink.

The pigment(s) or dyestuff used in the concentrate and inks of the invention should be chemically suitable for the end-use specification, e.g. an acidic pigment or dyestuff should not be adopted for a design requiring alkali resistance. In addition, the pigment or dyestuff should disperse readily in the selected vehicle system, ideally giving an ink with near Newtonian flow properties, which when reduced to the viscosity required in the printing press will give good gravure printability. Thirdly, the pigment should exhibit good dispersion stability, both as the ink is supplied and also at press viscosity, since recycled material may be stored for lengthy periods prior to reuse.

The gravure process will frequently require the same ink to be printed as a solid and as a tonal colour. It is therefore desirable that where pigment blends are adopted they should be of a similar particle size. This prevents the problem of the finer particle size pigment being preferentially printed out in the shallow tones

with a consequent variation in hue from the same ink in solid areas. The following are typical pigments to provide desired colouration.

Yellows and Oranges

Diarylide and monoarylide yellows are the most widely used.

Reds

Lake red C, Permanent Red 2B and the Lithol Red 4B and 6B toners find wide application due to their high tinctorial strength at economic cost. Care should be exercised with the 4B, 6B toners if a waterbased overprint varnish is to be applied, due to their partial solubility in water. With the exception of the Manganese 2B toner, all the above pigments have poor-moderate lightfastness and if an improvement in this property is required then the para and toluidine reds can be utilised.

Violets

PMTA and indanthrene violet are also most exclusively used although the latter generally gives inks with poor flow characteristics and its use is avoided where possible.

Greens

Phthalocyanine and PMTA greens are the most common, though great care should be taken with the former on long print runs as it can cause excessive wear of the chrome cylinder.

Whites

Titanium dioxide (rutile grade) is the generally adopted pigment. Grades produced by the sulphate process are preferred as the chloride grades tend to give cylinder wear problems. For certain applications, even sulphate grade rutile pigments can cause excessive wear and then either the anatase grade or preferably zinc sulphide is utilised, albeit with a decrease in opacity.

The ink concentrate or formulation optionally contains extender pigments, which are materials included to modify or extend the main, colour promoting pigment or dyestuff. The extender pigment may be employed to modify the colour and/or the opacity of the ink, or to enhance the miscibility of the main pigment or dyestuff with the other components.

The ink concentrate or formulation also typically contains other additives, such as plasticizers and/or waxes, that modify the physical properties, e.g. flow, of the concentrate or ink formulation, dependent on the projected conditions of use.

The preferred fluids for use as solvents according to the present invention boil in the range 100 to 120°C. Ideally, C7 and C8 paraffinic and naphthenic molecules predominate; for example the fluid preferably comprises from 70% to 100% of saturated aliphatic molecules containing 7 to 8 carbon atoms. In a particularly preferred solvent system the fluid has a density at 15°C in the range 0.70 to 0.75 g/cm^3, more especially a density of 0.72 to 0.74 g/cm^3.

The fluid should generally have a sulphur level as measured by ASTM D 4045) below 3 mg/kg, with sulphur levels below 10 wppm being preferred.

According to one aspect the present invention provides a gravure printing ink concentrate comprising from 45% to 60% of a fluid boiling in the range 80° to 120°C and comprising 45% to 70% paraffinic molecules and 30% to 55% naphthenic molecules (the total of paraffinic molecules and naphthenic molecules being 100%), from 10% to 30% of a resin and from 4% to 12% of a pigment.

The invention further provides a gravure printing ink comprising from 70% to 85% of an aliphatic fluid boiling in the range 80°C to 120°C and comprising 45% to 70% paraffinic molecules and 30% to 55% naphthenic molecules (the total of paraffinic and naphthenic molecules being 100%), from 9% to 15% of a resin and from 4% to 6% of a pigment.

The invention yet further provides a gravure printing ink concentrate comprising from 45% to 65%, eg 45% to 60%, of an aliphatic fluid boiling in the range 80 to 120°C comprising a mixture of paraffinic and naphthenic molecules derived from crude oil by distillation followed by hydrogenation and fractionation, from 10% to 30% of a resin and from 4% to 12% of a pigment.

In an even further embodiment the invention provides gravure printing ink comprising from 70% to 85% of an aliphatic fluid boiling in the range 80 to 120°C comprising a mixture of paraffinic and naphthenic molecules derived from crude oil by distillation followed by hydrogenation and fractionation, from 9% to 15% of a resin and from 4% to 6% of a pigment.

The percentages of the components mentioned in the four embodiments above are based in each case on the total weight of fluid, resin and pigment.

It is preferred that in the four embodiments set out above, the fluid boils in the range 100 to 120°C and that it contains at least 70% of aliphatic molecules containing 7 or 8 carbon atoms.

The invention further provides a gravure printing process employing a gravure printing ink as described above wherein after printing the solvent fluid is recovered and reused in the printing facility where the original printing is performed.

CLAIMS

1. The use as a solvent for gravure inks of an aliphatic hydrocarbon fluid boiling in the range of from 80°C to 140°C and comprising from 45 to 70 wt% paraffinic molecules and from 30 to 55 wt% naphthenic molecules, the combined weight of paraffinic molecules and naphthenic molecules being at least 90 wt% of the fluid.

2. The use according to claim 1 in which the fluid comprises from 45 to 60 wt% paraffinic molecules and from 40 to 55 wt% naphthenic molecules.

3. The use according to claim 1 or 2 in which the fluid comprises from 95 to 100 wt% paraffinic and naphthenic molecules.

4. The use according to any of the preceding claims wherein the fluid contains from 10-1000 wppm toluene.

5. The use as a solvent for gravure inks of an aliphatic fluid derived from crude oil and boiling in the range of from 80°C to 140°C and comprising a mixture of paraffinic and naphthenic molecules.

6. The use according to any of the preceding claims in which the fluid has a boiling range of no more than 40 degrees C

7. The use according to claim 6 in which the fluid has a boiling range of no more than 20 degrees C.

8. The use according to any of the preceding claims in which the fluid boils in the range of from 80°C to 120°C.

9. The use according to any of claims 1 to 7 in which the fluid boils in the range of from 100°C to 140°C

10. The use according to claim 9 in which the fluid boils in the range of from 100°C to 120°C.

11. The use according to any of the preceding claims in which the molecules are in the C_6 to C_9 carbon range.

12. The use according to claim 11 in which the paraffinic and naphthenic molecules are predominantly C_7 or C_8 molecules.

13. The use according to any of the preceding claims wherein the fluid has a sulphur level below 10 wppm, as measured by ASTM D-4045.

14. The use according to any of the preceding claims wherein the fluid boils in the range of from 100 to 120°C and comprises from 70% to 100% of saturated aliphatic molecules containing 7 or 8 carbon atoms.

15. The use according to any of the preceding claims wherein the fluid has a density at 15°C in the range of from 0.70 to 0.75 g/cm^3.

16. The use according to claim 15 wherein the density is in the range of from 0.72 to 0.74 g/cm^3.

17. A gravure ink concentrate comprising in weight %, based on the total weight of the concentrate :

pigment or dyestuff	4–12%
extender pigment	0–8%
resin	10–30%
fluid	40–60%
plasticizers and wax	2–10%

wherein the fluid is as defined in any of the preceding claims.

18. A gravure printing ink comprising in weight %, based on the total weight of

the ink:

pigment or dyestuff	4–6%
extender pigment	0–4%
resin	9–15%
fluid	70–85%
other additives optionally including plasticizers and wax	2–5%

wherein the fluid is as defined in any of claims 1 to 16

19. A gravure printing ink concentrate which comprises from 45 to 65wt% of an aliphatic fluid boiling in the range 80 to 120°C and comprising a mixture of paraffinic and naphthenic molecules derived from crude oil by distillation followed by hydrogenation and fractionation, from 10 to 30 wt% of a resin and from 4 to 12 wt% of a pigment, which percentages are based on the total weight of fluid, resin and pigment.

20. A gravure printing ink which comprises from 70 to 85 wt% of an aliphatic fluid boiling in the range 80 to 120°C and comprising a mixture of paraffinic and naphthenic molecules derived from crude oil by distillation followed by hydrogenation and fractionation, from 9 to 15 wt% of a resin and from 4 to 6 wt% of a pigment, which percentages are based on the total weight of fluid, resin and pigment.

21. An ink or a concentrate according to claim 19 or 20 wherein the fluid boils in the range 100 to 120°C and contains at least 70% of aliphatic molecules containing 7 or 8 carbon atoms.

22. A gravure printing process employing a gravure printing ink according to claim 20 or claim 21 wherein after printing a substrate in a printing facility, fluid is recovered from the ink and reused in the same printing facility.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/005700

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D11/02

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)
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 676 743 A (LEE ROBERT WEN [US]) 14 October 1997 (1997-10-14) claim 1 column 1, lines 42-45 column 1, line 54 - column 2, line 15 column 2, lines 19,20 column 2, lines 64-67 column 3, lines 20-40	1-22

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 September 2007	26/09/2007

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2007/005700

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5676743 A	14-10-1997	NONE	