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(54) Title: INK COMPOSITION

(57) Abstract

An ink jet ink especially for printing on to plain paper comprises a suspension in (a) a non aqueous solvent of (b) a disperse phase comprising: (i) a water-insoluble dyestuff which is insoluble in said solvent at the ink jet operating temperature and below; (ii) a water-insoluble resinous dispersant for the dyestuff which in the amount used is capable of forming a solution in the said solvent at the ink jet printer operating temperature, (iii) a polymeric binder to hold the dyestuff on the surface of the paper.

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INK COMPOSITION

This invention relates to ink compositions and more particularly to ink compositions for printing on plain paper using an ink jet printer, and a method of ink jet printing on paper. The invention is especially concerned with compositions suitable for use as inks in so-called "drop-on-demand" ink jet printers.

In ink jet printing, a fluid ink is forced under pressure, and sometimes at elevated temperature, through a very small nozzle in a printing head.

In one kind of printer, known as a "continuous" printer, ink droplets which are produced continuously are passed through a charging area where individual droplets receive an electrical charge in response to a signal and are directed towards a substrate to be printed. The droplets pass through an electrical field causing them to be deflected by an amount which is dependent on the intensity of the charge and the field. Droplets not required to form print on the substrate are directed to a by-pass gutter. Inks for use in such printers need to be conductive.

One proposal for a suitable ink composition for a DOD ink jet printer has involved the use of dyestuffs which are precipitated from solution in the solvent on contacting the substrate surface as a result of a change in pH of the dyestuff effected by reaction thereof with the substrate. However, this limits the choice of dyestuff and also involves the use of special papers.

An alternative approach has been the development of inks employing as the carrier a substance which is solid at room temperature. The inks are used as hot melts and solidification is achieved by cooling. However, such inks require expensive energy to convert them to the molten state and relatively large energy requirements to eject the drops from the printhead due to their high viscosity even when molten.

Another approach, described in our co-pending EP-A- 0403272, has involved developing an ink comprising a dispersion of dyestuff in a solvent containing a polymeric component which is soluble in the solvent when warm but insoluble at room temperature. With these inks, formation of the solid dot relies on precipitation of the polymer and dyestuff from the solvent on contact of the ink droplet with the cold substrate surface or during its trajectory from the printhead. While these inks do not require operating temperatures as high as the hot melt inks, they still require the use of heated printheads.

Good print definition quality requires *inter alia* (a) rapid formation of a solid colored dot from the ink composition, (b) concentration of the ink colorants on the surface of the paper (c) control of the spread of the dot of colour formed on the surface of the paper substrate from the ink droplet, and (d) uniformity of colour and colour density over the area of the solid dot formed from the droplet. Preferably, also, the print should not deteriorate as a result of the action of water or light.

It is also important, especially when it is intended for use in a DOD ink jet printer, that the ink be stable on standing or storage; not become concentrated by loss of solvent or form aggregates in the nozzle or at the orifice of the nozzle because this could lead to clogging of the nozzle itself or of the channel supplying the nozzle; and not form deposits around the periphery of the nozzle orifice during drop ejection.

In the ink droplet, the colour-generating component, or dyestuff, is generally associated with a liquid carrier, alternatively referred to as a solvent. Thus, rapid formation of the solid dot requires either rapid solidification of the solvent or rapid removal of the solvent from the colour dot on the paper, e.g. by rapid sorption of the solvent into the paper.

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The formulation of inks comprising a dispersion of dyestuff in a solvent for use in ink jet printers presents inherently conflicting requirements. For example, while it is desirable for the solvent to have a low volatility so as to minimise the risk of evaporation in the printhead nozzle, the rate at which the print dries can be enhanced by increasing the volatility of the solvent. Furthermore, for use on uncoated papers, it will be understood that if the dyestuff particles are too small, their tendency to pass through the interstices between the fibres forming the surface of the paper will increase, thereby reducing one or both of colour density and print definition. On the other hand, increasing the particle size will tend to increase the difficulty of achieving a stable dispersion, and the risk of clogging the nozzle, especially in DOD printers where the ink is held for long periods in the nozzle when that nozzle is inactivated.

A further problem is that of the viscosity of the ink because while a low viscosity is required to assist ink flow in the passages in the print head and ejection of the droplets from the print head, lowering the viscosity will generally increase the rate at which the droplet will spread over the paper surface and into the pores of the paper.

Even if these conflicting requirements are resolved satisfactorily, there remains the problem of achieving an acceptable colour density at a level of concentration of dye in the ink which can be maintained as a stable dispersion and with the ink having an acceptably low viscosity.

Thus, it is possible to employ the dyestuff in the form of particles which are sufficiently small for the ink to behave effectively as a liquid during drop ejection in a DOD ink jet printer and yet to achieve well defined print of good colour density. The ink is characterised by low viscosity at the shear rate effective during drop injection from the nozzle without risk of unacceptable spread of the colour content of the droplet over the paper surface.

In a preferred embodiment of the invention, the phase separation is assisted where the disperse phase comprising the combination of dyestuff, binder and dispersant is precipitated from the chosen solvent by contact with plain paper, e.g. due to the action of surface size or moisture present in the paper or due to the concentration effect caused by absorption of the solvent with the body of the paper. A test for one suitable form of this preferred embodiment of the ink is for the disperse phase of the ink to be precipitated by contact of the ink with water.

Volatilisation of the solvent is not essential for rapid drying of the dot since solvent removal may be achieved in other ways, e.g. by absorption into the substrate.

Also, as the dyestuff is insoluble in the solvent and remains associated with the dispersant and binder, it is not absorbed into the paper with the solvent and is substantially inhibited from spreading laterally over or through the paper fibres. Thus the colour content of the dyestuff is concentrated on the paper surface in the solid dot.

(ii) a water-insoluble resinous dispersant for the dyestuff which in the amount used is capable of forming a solution in the said solvent at the ink jet operating temperature; and

(iii) a polymeric binder to hold the dyestuff on the surface of the paper.

The ink of the present invention includes a disperse phase in which the dyestuff is associated with the resinous dispersant and the binder. As the tendency in ink jet printers is towards reduction in the nozzle size so as to improve printing definition and nozzle diameters of less than 50 μm or even less than 20 μm are contemplated, it becomes increasingly important not only that the dispersion is substantially stable but also that the particles are well dispersed, with a minimum of agglomeration. By means of the present invention, an ink is provided wherein the disperse phase is both well dispersed and substantially stable against precipitation and settling such that in ink jet printers of the kind described the ink will perform substantially as an uniform liquid.

When a drop of the ink is deposited on the surface of a paper substrate, the disperse phase comprising dyestuff, dispersant and binder separates from the solvent and becomes concentrated adjacent the paper surface while the solvent diffuses into the body of the paper. Aggregates of particles of the disperse phase form which tend to block the pores of the paper and hold the solids on the paper surface thereby forming the colour dot and fixing the dyestuff in the dot to the surface of the paper.

Thus, it is possible to employ the dyestuff in the form of particles which are sufficiently small for the ink to behave effectively as a liquid during drop ejection in a DOD ink jet printer and yet to achieve well defined print of good colour density. The ink is characterised by low viscosity at the shear rate effective during drop injection from the nozzle without risk of unacceptable spread of the colour content of the droplet over the paper surface.

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Furthermore, it has been found unexpectedly that the combination of the resinous dispersant and binder produces a print having a very good colour density at a lower dyestuff concentration, and hence lower viscosity, than would otherwise be required. In some cases, the colour density of print obtained from ink of the present invention matches those currently obtainable with offset printing, namely optical densities of as high as 1.6 as measured with a Macbeth reflection densitometer. Without wishing to be bound by this theory, it is believed that this is due to the fact that the unique combination of resinous dispersant and binder fills the pores between the fibres, so holding dyestuff on the surface, and limits dot spread, i.e. the tendency of the ink drops to spread after being deposited on the substrate surface.

By means of the present invention, therefore, inks are obtainable which have a viscosity which is low enough for ink jet printing, even on DOD ink jet printers, and have an acceptably low volatility and which are stable on storage and yet which are capable of producing print of high definition and colour density on plain paper.

Preferably, the ink composition exhibits shear thinning; that is, its viscosity is reduced with increase in shear rate.

The various components of the inks will now be discussed in greater detail.

or ambient conditions is less than 4%, and more preferably less than 2%, by weight. This is because in one preferred embodiment of the invention, the combination of dispersant, binder and dyestuff is chosen to be precipitatable from the chosen solvent by contact with water, e.g. by contacting a drop of the ink with a wet surface.

THE DYESTUFF

The dyestuff (which term may include certain pigments such as carbon black) is selected to be both water-insoluble and insoluble in the chosen solvent at the chosen operating temperature and below but such that the combination thereof with the resinous dispersant and binder forms a substantially stable dispersion in the solvent at the chosen operating temperature and below. A wide variety of dyestuffs is useful and in general the preferred dyes are found amongst those characterised as "pigment dyes" in The Colour Index.

Preferably the dyestuff will be of a primary subtractive hue. The dyestuff should be lightfast, and thermally stable even with repeated warming. The dyestuff should be water insoluble once applied to the substrate to prevent smearing upon contact with water-containing substances.

Dyestuffs which have been found to be useful include Pigment Green 7, Pigment Blue 15, Pigment Yellow 17, Pigment Yellow 83, Pigment Yellow 12, Pigment Black 2, Pigment Black 5, Pigment Black 7, Pigment Red 17, Pigment Red 23, Pigment Red 57 and Pigment Red 112 and the Ciba Geigy

The surface tension of the solvent will preferably be in the range 27 to 32 dynes/cm at 25°C and the boiling point is preferably greater than 150°C, and more preferably greater than 180°C, at atmospheric pressure.

The solvent may comprise a single component or a mixture.

Solvents which are particularly preferred because they are also readily absorbable into cellulosic fibres, and therefore do not have to rely on their volatility for removal from a dot printed on a paper substrate, are ethers of alkylene glycols and ethers of polyalkylene glycols. Specific examples include polypropylene glycol ethers and n-butyl ethers of ethylene glycol and poly(ethylene) glycol, especially the ethers of di- and tri- propylene glycol and the n-butyl ethers of diethylene glycol and triethylene glycol. Particularly preferred are the monomethyl ethers of di- and tripropylene glycol and the mono-n-butyl ethers of diethylene glycol and triethylene glycol.

Preferably, the solvent consists primarily or essentially of such a glycol ether or a mixture of such glycol ethers. That is, the ether or ethers will normally form at least 75% by weight, preferably at least 90% by weight, of the solvent.

By "non-aqueous" is meant that the solvent contains no more than about 5% by weight of water, including moisture absorbed from the atmosphere. Preferably, the solvent is free of any added water and it is also preferred that the solvent is such that the amount of moisture it is capable of absorbing from the atmosphere under normal operating

or ambient conditions is less than 4%, and more preferably less than 2%, by weight. This is because in one preferred embodiment of the invention, the combination of dispersant, binder and dyestuff is chosen to be precipitatable from the chosen solvent by contact with water, e.g. by contacting a drop of the ink with a wet surface.

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Microlith Series which includes Black, Red, Blue, Green, and Gold. Pigment Blue 15-6, Pigment Yellow 17 and Pigment Red 23 are the preferred dyestuffs.

Other useful dyestuffs include Cyan Blue BNF, Imperial Sacandaga Yellow and Lithol Rubine. These dyestuffs are especially suitable in combination with the preferred solvents, resin dispersants and polymer binders.

Additionally, certain carbon blacks are useful as pigments in the invention. Preferred carbon blacks are Continex N234 or N330 carbon black from Witco Chemical Corp, Regal 250R from Cabot Carbon and Chevron acetylene black.

Mixtures of dyestuffs may be used.

It is a feature of the invention that good print definition and colour density are obtained even where the dyestuff particles are small enough to pass through the interstices between fibres of the surface of a paper substrate. Thus the particle size of the dyestuff may be 1.5µm or less and is preferably not greater than 1.0µm, more preferably not greater than 0.5µm, still more preferably not greater than 0.3µm.

It is also preferred that the specific gravity of the dyestuff is close to that of the chosen solvent since this reduces the likelihood of precipitation on standing.

dispersants sold by BYK Chimie of Germany under the trade names Anti-Terra 204, 207 and P and Disperbyk, dispersants sold by Efka Chemicals BV of Holland under the tradename "Efka", dispersants sold by ICI under the tradename "Solsperse" and AB dispersants sold by DuPont under the tradename "Elvacite". It will be understood, however, that not all resins within the classes listed are necessarily dispersants for all combinations of dyestuffs, solvents and binders.

Preferred resinous dispersants give a solution in the chosen solvent which, at the concentration of the dispersant employed in the ink, has a viscosity not very much greater than that of the solvent alone.

Preferably, the viscosity of the solution of the dispersant in the solvent is not greater than 15cps.

Very good results are obtained with "Beckacite" synthetic rosin esters and with thermoplastic acrylic-based resins such as Acryloid DM-55, (also know as Paraloid DM 55), marketed by Rohm and Haas.

THE BINDER

The binder is chosen to form a uniform coating on, and adhere well to, the chosen substrate, especially cellulose fibres, should be optically clear and should hold the selected dyestuff on the substrate surface under ambient conditions. Preferably, the binder is such that it not only coats cellulose fibres but also bridges interstices between cellulose fibres on a paper surface. In the ink composition, the binder should associate with the disperse phase and in that sense must be compatible with the resinous dispersant.

with plain paper, e.g. due to action of the water and/or surface size, e.g. clay, in the paper or because of the concentration effect caused by absorption of the solvent into the paper. A convenient test for a suitable dispersant is to determine whether it is precipitated from a solution thereof in the desired concentration in the chosen solvent when the solution is contacted with plain paper or with water. Thus, while the dispersant must be soluble in the chosen solvent, and should also be soluble in mixtures of the solvent and small quantities of water such as may be absorbed from the atmosphere on standing, in one embodiment of the invention it is chosen such that it separates from the solvent on addition of a larger concentration of water. Such water sensitivity reduces still further the risk of undesired dot spread.

The dispersant may comprise a single component or a mixture.

Examples of resin classes from which suitable resinous dispersants may be chosen are natural resins such as alcohol soluble gums, synthetic analogues of natural resins such as synthetic rosin esters and alcohol-soluble polysaccharides, and acrylic resins. Examples of suitable natural resins include gums Kauri, Copal, Mastic and Sandarac. Examples of synthetic analogues of natural resins include synthetic rosin esters such as those sold as "Beckacite" by Reichhold. Other examples are cellulose esters, e.g. cellulose acetate propionate and cellulose acetate butyrate; hydroxyalkyl celluloses and

dispersants sold by BYK Chimie of Germany under the trade names Anti-Terra 204, 207 and P and Disperbyk, dispersants sold by Efka Chemicals BV of Holland under the tradename "Efka", dispersants sold by ICI under the tradename "Solsperse" and AB dispersants sold by DuPont under the tradename "Elvacite". It will be understood, however, that not all resins within the classes listed are necessarily dispersants for all combinations of dyestuffs, solvents and binders.

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It is not essential for the binder to be soluble in the solvent at ambient temperature. Indeed, in one form it is preferred that in the amount in which it is used in the ink it is insoluble or substantially insoluble at ambient temperature but is at least partly, and preferably entirely or substantially entirely, soluble at elevated temperature; for example having a cloud point just above room temperature (e.g. in the range 25 to 50°C). The use of such binders provides further control of dot spread and favours good dot formation.

Where the ink jet printer operating temperature is above ambient temperature, it is preferred that the binder is at least partly in solution in the solvent at said operating temperature but is insoluble or substantially insoluble in the solvent at room temperature, thereby allowing the use of the temperature range to assist control of dot spread.

Alternatively or additionally, it is preferred that the binder be such that the disperse phase containing the binder, the chosen dispersant and the chosen dye separates from the solvent when a droplet of the dispersion contacts a plain paper surface, e.g. due to action of water or size in the paper.

A single polymer or a mixture of polymers may be used as the binder.

The amount of dispersant required will depend upon the choice of the solvent and dyestuff and also the particle size of the dyestuff. If too little is used, dispersion will be incomplete or the resultant dispersion will be unstable. However, there is a concentration of dispersant above which no further dispersive effect will be obtained. This level of concentration is that at which the viscosity of the dispersion of chosen dye and dispersant in the selected solvent is a minimum. Nevertheless, in the case of some resinous dispersants, it has been found that if the dispersant is included in an amount in excess of the level of concentration that yields the minimum viscosity, the excess can act as, or as part of, the binder.

Accordingly, it will be understood that the resin chosen as the dispersant may in some circumstances also act as a binder where it is employed in an amount in excess of that at which the viscosity of the combination of solvent, dye and resin reaches a minimum.

The amount of dispersant that gives the minimum viscosity for a particular composition of dye and solvent may be determined by measuring the viscosities of a number of such compositions containing the dispersant in varying concentrations and plotting a graph of measured viscosity against concentration of dispersant.

It is likewise believed that in some cases, the resin chosen as the binder may also assist dispersion. It may also assist in stabilising the dispersion against settling.

Other resins which may be employed as binders include acrylic resins such as those marketed as "Elvacite" by DuPont and "Degalan" by Degussa; carboxylated acrylic resins such as those marketed as "Surcol" by Allied Colloids; amino resins, e.g. melamine, urea and benzoguanamino-based resins, such as those marketed under the tradename "Beetle" by British Industrial Plastics Limited; polyvinyl butyrals, phenolics, nitrocellulose and polyisobutylene. It will be understood that not all resins within these classes will necessarily be suitable with all combinations of dyestuff, dispersant and solvent.

The effect of the binder is to hold the dyestuff on the surface and contain dot spread thus enabling print of higher optical density to be achieved for a given concentration of dyestuff. Alternatively, it enables the same level of optical density to be achieved at a lower dyestuff concentration, thereby enabling a reduction in the viscosity of the ink. For example, replacing part of the dyestuff with the same weight of preferred ethylene/vinyl acetate copolymer increases optical density.

PROPORTIONS OF INGREDIENTS

The concentrations of the various components in the ink may be varied to suit particular requirements and end uses.

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It is likewise believed that in some cases, the resin chosen as the binder may also assist dispersion. It may also assist in stabilising the dispersion against settling.

The amount of dispersant employed will depend upon the nature, particle size and concentration of the dyestuff and will generally be in the range of 1 - 5 parts per part of dyestuff, by weight. In general, where the resin is selected from natural resins and acrylics it will be employed as a dispersant in an amount of from about 2 to about 12% of the total weight of the ink. Within this range, the amount will generally be in the range 2 to 8% for reds, yellows and blues but higher amounts, e.g. 4 to 10%, may be required for carbon black. If lower amounts are used, an adequate dispersive effect may not be achieved. However, where it is desired for the same resin to act also as, or as part of, the binder, larger amounts may be employed. Where a mixture of ethylene/vinyl acetate copolymer and acrylic resin or natural resin is employed as the dispersant, as a general rule of thumb it can be said that 1 part of the copolymer may replace 2 parts of natural resin or acrylic, by weight. However, the amount of dyestuff that may be included in the ink at the same viscosity is increased with increase in the ratio of natural resin or acrylic to ethylene/vinyl acetate copolymer in the dispersant.

If the binder concentration is below about 1%, optical density may be adversely affected e.g. due to fibre showthrough. The maximum amount of binder that may be employed is generally controlled by viscosity considerations since increasing the amount of binder generally increases the viscosity of the ink, although the size of the increase depends to some extent on the nature of the binder. In general, therefore, it will be undesirable to use more than 4% although larger amounts, even up to 10%, may be acceptable in some cases.

Thus the total amount of resin employed in the ink as dispersant and as binder will generally be in the range of 3 to 16% by weight of the ink.

The amount of dyestuff employed will normally be in the range 2 to 5% by weight of the ink although larger or smaller amounts may be used if desired. It is a feature of the present invention, however, that even at these low levels of concentration, print of excellent colour density is achievable. Colour densities of up to as high as 1.6 are achievable with the darker colours such as magenta, red, blue and black.

Preferably, the solvent forms at least 80% of the ink composition, more preferably 95 to 83%, by weight. For most formulations, the solvent will form 93% to 84% by weight of the ink composition.

It will be understood that the ink composition may also include further components conventionally employed in inks, e.g. surfactants, drag-reducers, etc.

Whereas inks according to the invention may be formulated for operation at ambient conditions, they may also be employed at elevated temperatures. Operation at a moderately elevated temperature, e.g. 30 to 60°C, preferably 50 to 55°C, has the advantage of permitting greater control over operating conditions without being hazardous.

Where the inks are intended for use at such elevated temperatures, it will be understood that somewhat higher concentrations of dye, dispersant and/or binder may be employed or alternatively the viscosity of the ink at the operating temperature may be lower, thereby reducing energy requirements and permitting the use of lower actuation voltages and less expensive drive circuits.

Print with very good definition and colour density is obtainable from the use of inks according to the invention in ink jet printers. In particular, the dot spread is low, especially where the dispersant is a natural resin or acrylic resin, and the colour density is higher than that normally obtainable with the same concentration of dyestuff in the absence of the binder.

Inks according to the invention may be prepared by any suitable process. In one method, the binder, dispersant and dyestuff are dispersed in a small amount of solvent, e.g. by milling, and the resultant concentrated dispersion is then let down to the required concentration by addition of more solvent.

The invention is illustrated by the following Examples in which TPM means tripropylene glycol monomethyl ether.

Acryloid DM 55 (also marketed as Paraloid DM 55) is an acrylic copolymer marketed by Rohm and Haas.

Elvax 170 and Elvax 40-W are ethylene/vinyl acetate copolymers marketed by Du Pont.

Elvacite 2013 is an acrylic resin marketed by Du Pont.

Vynathene 90500 is an ethylene/vinyl acetate copolymer marketed by Quantum.

Beckacite is a synthetic resin ester sold by Reichhold.

Efka 47EA is a resinous dispersant sold by Efka Chemicals BV of Holland.

All the colorants used in the following Examples had particle sizes of 0.5 μm or less and in all the Examples, the solvent was carefully dried before use.

EXAMPLE 1

3g of Acryloid DM-55 were dissolved in 20 ml of warm (50-60°C) water-free TPM by stirring for 30 minutes. To this solution was added 2 g of Heliogen Blue L-6700 (BASF) and the resultant mixture stirred for 4 hours at 60°C. The dispersion so obtained was then allowed to cool to room temperature while stirring over a period of 45 minutes, then reheated to 60°C to form slurry 'A'.

0.3 g Vynathene 90500 and 0.8 g ELVAX 170 were slurried in 10 ml TPM at 120°C. After 24 hours the hazy solution so obtained was allowed to cool to 60°C and was then added over a period of 10 minutes to slurry 'A'. The mixture was stirred for a further 16 hours, then diluted to 70 ml with dry TPM.

The resultant ink had a viscosity of 250 to 150cps at shear rates of 8 to 80 sec^{-1}, gave good dots on paper and was stable, meaning that no signs of sedimentation or settling were observed, even after several months.

EXAMPLE 2

3 g Acryloid DM-55 were dissolved in 20 ml warm (50-60°C) TPM by stirring for 1 hour. 1.75 Cromophtal yellow 8 G (Ciba-Geigy) was added to this solution and the whole stirred at about 55°C for 4 hours. The dispersion so obtained was then allowed to cool to room temperature and stirred for 1 hour before reheating to 55°C. To this disperson was added a warm solution obtained by dissolving 1 g ELVAX 40-W in 10 ml TMP 120°C over 3 hours and then allowing it to cool to 60°C. The resultant slurry was stirred for 72 hours and then let down to 50 ml with dry TPM.

The resultant ink was stable, gave very good dots on bond paper and had a viscosity of 50 to 30cps as the shear rate was increased from 8 to 80 sec^{-1}.

EXAMPLE 3

The procedure of Example 2 was repeated but using 1 g ELVAX 170 in place of the ELVAX 40-W. The solution of ELVAX in TPM was heated for 24 hours at 120°C and was still cloudy when added to the slurry of the Cromophtal 8G. After being let down to 50 ml with more TPM this ink also gave very good dots, and had a viscosity of 80 to 30cps at shear rates of 8 to 80 sec^{-1} and was stable.

EXAMPLE 4

4 g Acryloid DM-55 were dissolved in 17 ml of dry, warm (50-60°C) TPM by stirring for 1 hour. To this solution was added 2.5 g Heliogen Blue L 6700 (BASF) and the slurry so obtained was stirred at 55°C. 1 g Vynathene 90500 dissolved in 10 ml TPM by stirring at 60°C was then added to the slurry and the whole stirred for 24 hours at 60°C. It was then allowed to cool and diluted to 50 ml with more TPM.

This ink showed Newtonian behaviour from 300 to 3000 sec^{-1} with a viscosity of 43cps at these shear rates. The ink showed no tendency to settle, even after standing for over 2 months and gave print dots of excellent definition and colour density. By way of comparison, an ink having the same composition but excluding the Acryloid DM-55 would show signs of separation within a short period of time and also signs of gelling. Print from an ink having the same composition but excluding the Elvax 40-W would have poorer definition with a tendency to wick through the paper.

EXAMPLE 5

2.65 g Acryloid DM-55 were dissolved in 16 ml dry TPM at 60°C by stirring for 1 hour. 1.5 Irgalite Red RBS (Ciba Geigy) was added and slurried at 60°C for over 4 hours. To this slurry was added a warm solution obtained by dissolving 0.85 g ELVAX 40-W in 10 ml dry TPM at about 100°C. The resultant slurry was stirred for 72 hours at 60°C, and was then cooled and let down to 50 ml with more TPM. The resultant ink had a viscosity of 14cps at a shear rate of 3000 sec^{-1}, showed very little tendency to settle over a period of more than 2 months and gave dots of good optical density.

EXAMPLE 6

To 20 ml dry TPM at 60°C were added 4 g Acryloid DM-55 and the resultant mixture was stirred for 30 minutes to form a solution.

2 g Heliogen Blue L 6700 (BASF) were added and the resultant dispersion stirred for 16 hours at 60°C. While stirring the dispersion was cooled to room temperature, then stirred at room temperature for 1 hour and then reheated to 60°C while stirring. 1 g ELVAX 40-W was then added and the mixture stirred at 60°C for a further 72 hours. It was then cooled to room temperature and let down to 50 ml with more TPM. This ink had a viscosity of 22cps at a shear rate of 3000 sec^{-1}, gave good dots on bond paper and was stable.

EXAMPLE 7

The procedure of Example 6 was repeated using 1.75 g Irgalite Red RBS (Ciba Geigy) in place of the Heliogen Blue, and then stirring for 4 hours before reducing the temperature to 60°C. This ink, after being let down to 50 ml, had a viscosity of 26cps at a shear rate of 3000 sec^{-1} and gave excellent dots on bond paper. The ink showed very little settling with time.

EXAMPLE 8

The procedure of Example 7 was repeated but using 2 g carbon black N234 (Witco) as dyestuff. The resultant ink had a viscosity of 19cps at a shear rate of 3000 sec^{-1}, gave good dots, and did not settle on standing.

EXAMPLE 9

To a solution of 2.5 g of Copal A in 12 ml of TPM were added 12 ml of dry TPM and 1.5 g Irgalite Red, RBS (Ciba Geigy). The resultant slurry was heated to 60°C, stirred for 4 hours at 60°C, allowed to cool to room temperature while stirring and then reheated to 60°C while stirring. A solution of 1 g ELVAX 40-W in 10 ml TPM was added to the resultant slurry and the mixture stirred overnight, and then cooled and let down to 50 ml with more TPM.

The resultant ink gave good dots, had a viscosity of 25cps at 3000 sec^{-1} shear rate, and showed little or no tendency to settle.

EXAMPLE 10

The procedure of Example 9 was used with a solution of 3 g Beckacite (Reichhold) in 20 ml TPM in place of the Copal A solution. The ink produced had a viscosity of 27cps at 3000 sec^{-1} shear rate, gave good dots, and also showed little or no tendency to settle.

Print from the black, red and blue inks of Examples 1 and 4 to 10 above exhibited optical reflection densities in the range 1.4 to 1.65.

EXAMPLE 11

0.5 g Vynathene 90500 and 2 g Acryloid DM-55 were dissolved in 20 ml of dry TPM by stirring and heating to 60°C. While at this temperature and with continued stirring 1.75 g of N330 carbon black (Witco) were added and stirred for 48 hours. A warm (60-80°C) solution of 1.6 g ELVAX 40-W in 10 ml of TPM was then added and the resultant mixture stirred for 6 hours, allowed to cool, and diluted to 50 ml with more TPM. The resultant ink was non-Newtonian in viscosity, gave well defined dots of good optical density, and did not settle on standing.

EXAMPLE 12

1 g Vynathene 90500 and 2 g Acryloid DM-55 were dissolved in 20 ml dry TPM in the manner described in Example 11. 2 g Heliogen Blue 6700 (BASF) was added and the mixture stirred warm for 8 hours. Then 1.75g ELVAX 40-W as a solution in 10 ml TPM was added and the resultant slurry stirred warm for 8 more hours, cooled, and diluted to 50 ml with more TPM. The resultant ink was non-Newtonian, gave very good dots, and did not show any settling in 4 days.

EXAMPLE 13

0.5 g cellulose acetate butyrate 500.1 (Eastman) and 1 g Acryloid DM-55 were dissolved in 20 ml warm dry TPM. 1.6 g Irgalite Red RBS (Ciba Geigy) were then added and the mixture stirred for 4 hours. A solution of 1.6 g ELVAX 40-W in TPM was then added and the whole stirred for 6 hours, allowed to cool and let down to 50 ml with TPM. The resultant ink was non-Newtonian, gave very good dots, and did not settle on standing.

EXAMPLE 14

This Example and Example 15 illustrate the use of Paraloid DM 55 as a binder.

To 5g of carbon black Regal 250R (particle size 0.1-0.3 μm) were added 8.8g of a preformed solution of 2.9g Efka 47 EA dissolved in TPM and 20g of a solution of 6g Paraloid DM 55 also dissolved in TPM and mixed with a high intensity mixer for 10 minutes. 90g of zirconia beads (of diameter 1-2 mm) were added to this premix and milling carried out for 40 minutes. The beads were then removed from the mixture by sieving and the mixture diluted with high intensity mixing to produce an ink with 5% carbon content.

The viscosity of the ink was measured as 14cPs at a shear rate of $37s^{-1}$ (Brookfield LV) and 55cPs falling to 15cPs at shear rates of 5 and $6000s^{-1}$ respectively. (Bohlin CS Rheometer). The ink was stable and gave dots having a sharply defined edge and an optical density of about 1.3 to 1.45.

EXAMPLE 15

The method of Example 14 was repeated using 7% Regal 250R; 3% Heliogen blue L6700F; 3.9% Efka 47EA and 6% Paraloid DM 55.

This ink gave a printed optical density in excess of 1.25 and had a viscosity of 65cPs falling to 30cPs at shear rates of 10 and $3,500s^{-1}$ respectively.

EXAMPLE 16

A black ink was prepared by dissolving 4g of Acryloid DM 55 in 20ml of warm (50-60°C) water-free tripropylene glycol monomethyl ether (TPM) while stirring and then, while maintaining the temperature and with additional stirring adding 2g of N330 carbon black (Witco). To the mixture so formed was added a warm (60-80°C) solution of 1.75g of Elvax W in 10ml of TPM and the whole was stirred for a further 72 hours and then allowed to cool and diluted to 50ml with more TPM.

Red and blue inks were also prepared. The red ink was prepared following the same procedure as that of the black ink but using 2g of Acryloid DM 55, 2g of Elvax W and, as the dyestuff, 1.8 g of Irgalite Red 2BX RBS (Ciba Geigy). The blue ink was prepared following the same procedure and using the same quantities of materials as for the red ink but using 2g of Heliogen Blue L6700 (BASF) as the dyestuff.

All the inks of this Example demonstrate shear thinning.

Example 17

An ink was prepared from TPM and containing 5% by weight of Mogul L carbon black (obtained from Cabot Corporation) and 9% by weight of EFka 47EA. In this composition, it was found by experiment that the minimum viscosity was obtained at concentration of the EFka 47EA of 2.5% ± 0.5%. Thus, this Example illustrates the use of the EFka as both dispersant and binder, with about 6.5% providing the binder

function. The viscosity of the ink was 22 cPs at 12 rpm, measured on a Brookfield LV viscometer. Dots formed from the ink had a well defined edge.

Example 18

An ink was prepared from TPM containing 5% Regal Black 250R, 2.6% EFka 47EA and 3% Elvacite 2013, by weight. Experiment established that this amount of EFka 47EA alone was inadequate to achieve good dispersion of the colorant. 3.1% of the EFka was found to be required to achieve the minimum viscosity. Thus, in this Example, some of the Elvacite has the function of dispersant while the balance acts as binder limiting dot spread. Dots formed from the ink had a well-defined edge.

Claims

1. An ink jet ink composition comprising a suspension in

(a) a non aqueous solvent of (b) a disperse phase comprising:

(i) a water-insoluble dyestuff which is insoluble in said solvent at the ink jet operating temperature and below;

(ii) a water-insoluble resinous dispersant for the dyestuff which in the amount used is capable of forming a solution in the said solvent at the ink jet printer operating temperature,

(iii) a polymeric binder to hold the dyestuff on the surface of the paper.

2. A composition as claimed in Claim 1 in which the solvent has an evaporation rate at 25°C and atmospheric pressure less than one-tenth that of butyl acetate, a viscosity not exceeding 20cps at 25°C when measured using a Brookfield LV Viscometer with a No. 1 spindle at a shear rate in the range 8 sec^{-1} to 80 sec^{-1}, a surface tension in the range 27 to 32 dynes/cm at 25°C and a boiling point above 150°C.

3. A composition as claimed in Claim 1 or Claim 2 wherein the solvent consists essentially of at least one ether selected from ethers of alkylene glycols and ethers of polyalkylene glycols.

4. A composition as claimed in Claim 3 wherein said at least one ether is selected from monomethyl ethers of dipropyleneglycol and tripropylene glycol and n-butyl ethers of diethylene glycol and triethylene glycol.

5. A composition as claimed in any one of Claims 1 to 4 wherein the dispersant is one which, in the concentration employed, will precipitate from a solution thereof in the chosen solvent on contact with plain paper.

6. A composition as claimed in any one of Claims 1 to 4 wherein the dispersant is one which, in the concentration employed, is precipitated from solution in the chosen solvent by the contact with water.

7. A composition as claimed in any one of Claims 1 to 6 wherein the dispersant is selected from natural resins, synthetic analogues of natural resins, acrylic resins, cellulose esters, hydroxyalkyl celluloses, dispersants sold by ICI under the tradename "Solsperse", dispersants sold by DuPont under the tradename "Elvacite" and dispersants sold under the tradename "Efka" by Efka Chemicals BV.

8. A composition as claimed in any one of Claims 1 to 7, in which the binder is insoluble or substantially insoluble in the solvent at ambient temperature but at least partly soluble in said solvent at elevated temperature.

9. A composition as claimed in any one of Claims 1 to 8 in which a solution of the binder in the solvent has a cloud point just above room temperature.

10. A composition as claimed in any one of Claims 1 to 9 in which the binder is selected from an ethylene/vinyl acetate copolymers, acrylic resins, carboxylated acrylic resins, amino resins, polyvinyl butyrals, phenolics, nitro cellulose and polyisobutylene.

11. A composition as claimed in Claim 10 in which the binder is selected from ethylene/vinyl acetate copolymers containing 40 to 50% by weight vinyl acetate.

12. A composition as claimed in any one of claims 1 to 11 wherein the disperse phase is precipitated by contact of the ink with water.

13. A composition as claimed in any one of claims 1 to 11 wherein the disperse phase is precipitated by contact of the ink with plain paper.

14. A composition as claimed in any one of Claims 1 to 13 wherein the dyestuff is selected from pigment dyes.

15. A composition as claimed in any one of Claims 1 to 14 wherein the dyestuff has a particle size of 0.5μm or less.

16. A composition as claimed in any one of claims 1 to 15 containing from 2 to 5% by weight of dyestuff.

17. A composition as claimed in any one of claims 1 to 16 wherein the dispersant is present in an amount of from 1 to 5 parts per part of dyestuff, by weight.

18. A composition as claimed in any one of claims 1 to 17 containing from 2 to 12% by weight of dispersant.

19. A composition as claimed in any one of claims 1 to 18 containing from 1 to 4% by weight of binder.

20. A composition as claimed in any one of Claims 1 to 19 containing from 84% to 93% by weight of solvent.

21. A composition as claimed in any one of claims 1 to 20 but wherein the dispersant is employed in an amount in excess of that which yields the minimum viscosity for the dispersion thereof with the chosen dyestuff and solvent, the excess amount comprising at least part of the binder.

22. A composition as claimed in Claim 1 comprising by wei ght

84 to 93% of tripropylene glycol monomethyl ether

2 to 12% of acrylic resin, or mixture of acrylic resin and ethylene/vinyl acetate copolymer having a cloud point in said solvent below ambient temperature, as dispersant

1 to 4% of at least one ethylene/vinyl acetate copolymer containing 40 to 50% by weight vinyl acetate as binder 2 to 5% of dyestuff C to 2% of water the total adding up to 100%.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 92/00055

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: C 09 D 11/00

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[5]	C 09 D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	DE, A, 2 136 055 (A.B. DICK CO.) 27 January 1972 (27.01.72), see totality. --	1
A	EP, A1, 0 386 349 (AM INTERNATIONAL INCORPORATED) 12 September 1990 (12.09.90), see totality (cited in the application). --	1
A	EP, A1, 0 403 272 (XAAR LIMITED) 19 December 1990 (19.12.90), see pages 3-5 (cited in the application). --	1
A	EP, A1, 0 408 333 (XAAR LIMITED) 16 January 1991 (16.01.91), see pages 4,5	1

* Special categories of cited documents: [10]

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

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"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

"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

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
02 April 1992	06.05.92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	D. Haas

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages	Relevant to Claim No.
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ANHANG — ANNEX — ANNEXE

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

to the International Search Report to the International Patent Application No.

au rapport de recherche international relatif à la demande de brevet international n°

PCT/GB92/00055 SAE 55369

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsibilité de l'Office.

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