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(54) Title: INK JET PRINTER INK COMPOSITION

(57) Abstract

Ink jet printer ink composition comprising a dispersion of pigment in a diluent and wherein the maximum volume packing fraction of the disperse phase is not greater than 0.25 at 30 °C. Where other solids are present in the disperse phase in addition to the pigment, the value for maximum volume packing fraction applies to the total solids content of the disperse phase. Where the pigment is the only component of the disperse phase, the disperse phase should form more than 7 % but not more than 25 % by weight of the ink. Where the ink includes a component which is dissolved in the diluent, the maximum volume packing fraction of the components of the composition other than the diluent should not exceed 0.45.

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INK JET PRINTER INK COMPOSITION

This invention relates to pigment 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; however it is anticipated that the inks may also be suitable for use in other applications.

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 then 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.

In another kind of printer, known as a "drop-on-demand" (DOD) printer, the ink droplets are expelled from the nozzle of a print head only when required during the printing process. Drop-on-demand printers can use an electrostatically accelerated ink jet or droplet sequences ejected by pressure impulse actuation. In the latter kind of DOD printer, each drop of ink is individually ejected from a nozzle by means of pressure

pulses induced e.g. by use of a piezo-electric actuator acting on the ink in the channel supplying the nozzle or by generation of a vapour bubble in response to a thermal pulse.

For use in a DOD ink jet printer, it is important that the ink be stable on standing or storage. In particular, on standing it should not become concentrated through loss of diluent. Nor should it 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. It should also not form deposits around the periphery of the nozzle orifice during drop ejection.

Because specially coated papers are expensive, it is generally accepted that ink jet printer inks should be capable of producing print on plain, ie. uncoated, paper substrates which are at ambient temperatures. Moreover, the resultant print is expected to be well-defined and of good colour density despite the fibrous nature of the substrate.

Good print definition quality requires *inter alia* (a) rapid formation of a solid coloured dot from the ejected droplet of 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.

In the ink droplet, the colorant is generally associated with a liquid diluent sometimes referred to as a solvent and it has been assumed that to achieve the desired rapid

formation of the solid dot requires either rapid solidification of the diluent, e.g. by cooling, or rapid removal of the diluent from the colour dot on the paper, e.g. by evaporation or rapid sorption of the diluent into the paper. At the same time, however, it is desirable to control the sideways spread of the droplet after it has landed on the paper. It will be understood that these requirements are to some extent conflicting because sorption of the diluent into the paper will generally involve some sideways wicking.

In one form of ink formulation for an ink jet printer, the ink is a dispersion of finely divided colorant in a liquid diluent. However, the formulation of such inks presents inherently conflicting requirements. For example, while it is desirable for the diluent 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 diluent. Furthermore, for use on uncoated papers, it will be understood that if the particles of colorant 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 may be static in the nozzle for long periods during which 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, thus adversely

affecting both the colour density and definition of the print dot.

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

Our co-pending European patent application 90307571.1, published as EP-A-0408333, describes a plain paper ink formulation comprising a non-aqueous solvent (i.e. diluent) and, dispersed therein, an amount of resin which is capable of forming a solution in said solvent at a temperature in the range of 20 to 35°C, and a colorant which at said temperature is bound to or soluble in said resin but substantially insoluble in the solvent. The purpose of the resin is to bind the colorant to the cellulose of the paper to obtain a print dot of good definition and colour density from an ink containing colorant in the form of very small dispersed particles.

Our International patent publication WO 92/12209 describes a formulation which includes a water insoluble colorant which is insoluble in the solvent (i.e. diluent), a water insoluble resinous dispersant for the colorant which is soluble in the diluent and a polymeric binder. When a drop of this ink is deposited on the surface of a paper substrate, a phase comprising colorant, dispersant and binder separates from the diluent and becomes concentrated adjacent the paper surface while the diluent diffuses into the body of the paper. Aggregates of particles of this 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 colorant in the dot to the surface of the paper. This enables the employment of colorant 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 achieve well defined dots of good colour density.

It is believed that this is due to the fact that the combination of resinous dispersant and binder fills the pores between the fibres, so holding colorant on the surface, and limits dot spread, ie. the tendency of the ink drops to spread after being deposited on the substrate surface.

However, with the trend towards higher print definition, which means more nozzles per inch and thus smaller nozzle sizes, and for certain specialised applications such as in plain paper facsimile machines, still further improvements in the quality of the print, and especially the colour density of the print dot, are desirable.

According to the present invention, we have found that such further improvement in print quality can be achieved by means of an ink jet printer ink composition which at ambient temperatures is in the form of a dispersion having a disperse phase of finely divided solids in a liquid diluent and wherein the colorant is in the disperse phase and the maximum volume packing fraction of the disperse phase is not greater than 0.25 at 30°C.

For the purposes of this specification it is to be understood that ambient temperatures means temperatures in the range 15 to 30°C.

Also for the purposes of this specification, the colorant in the disperse phase is hereinafter referred to as pigment. In accordance with one aspect of the invention, which is particularly apposite where the pigment is carbon black, the pigment may form the disperse phase. In another aspect of the invention, however, the disperse phase may also include other components, in particular extenders, that are insoluble in the diluent at ambient temperatures. In this embodiment it is the totality of pigment and other particles which must have a maximum volume packing fraction less than 0.25.

In at least the first mentioned embodiment, the pigment should form more than 7% by weight, based on the weight of the ink. In general, however, it should not form more than 25% by weight.

It has been found that the inks according to the invention exhibit a high rate of increase of viscosity with increase in concentration of the disperse phase, e.g. as the diluent volatilises or separates from the droplet after the droplet has been deposited on the substrate on which the print is to be formed (by, for example, absorption into the substrate), thereby leading to more rapid solidification of the dot formed from the droplet, reduced drop spread, a reduced level of penetration of pigment below the surface of the substrate and thus a higher concentration of pigment in the dot and increased depth of colour.

By maximum volume packing fraction (MVPF) we mean the volume fraction ϕ_m, of the disperse phase where the viscosity tends to infinity; i.e. solid-like rather than liquid-like behaviour is observed due to the close packing and interaction of the solid particles

forming the disperse phase. This can be determined by measuring the rheological properties, including viscosity, of formulations having a range of concentrations of the disperse phase. A useful theoretical model which may be used to model the change in viscosity of a colloidal dispersion upon concentration is that due to Krieger and Dougherty [Krieger, I.M. and Dougherty, T.J., A Mechanism for Non-Newtonian Flow in Suspensions of Rigid Spheres, Transactions of the Society of Rheology, 3 (1959) 137-152]. This theory states that the viscosity of a dispersion can be given by the relationship

$$\eta = \eta_o(1-\phi/\phi_m)^{-[\eta]\phi_m}$$

where η_o is the viscosity of the diluent, ϕ is the solid colloidal particle volume fraction, ϕ_m is the maximum volume packing fraction and $[\eta]$ is a dimensionless parameter referred to as the intrinsic viscosity. From the above equation it can be seen that $\eta \rightarrow \infty$ as $\phi \rightarrow \phi_m$. For a real system however, it is possible to measure an apparent viscosity when $\phi > \phi_m$ with a suitable rheometer, although solid-like behaviour (which can also be measured) will dominate. It is also possible therefore to define ϕ_m as the point at which solid-like behaviour dominates over liquid-like behaviour as ϕ is increased.

The intrinsic viscosity $[\eta]$ and the MVPF can be determined by preparing a range of dispersions having different diluent contents. These dispersions should ideally range from pure diluent through to solid-like systems. This will eliminate the need to perform extrapolations with the data. The rheological properties of each dispersion sample can be measured with a rheometer such as a "Bohlin CS" [Bohlin Instruments Division, Metric Group Ltd., Love Lane, Cirencester, Gloucestershire GL7 1YG, UK] with a "CP 4/40" cone and plate measuring system at a temperature of 30°C. It is convenient to measure

the viscosity of the dispersion samples under conditions of constant stress. For Newtonian systems the choice of stress is not critical. However we have found that a value of not more than 10Pa is required to prevent invalid viscosity measurements due to secondary flow (turbulence) in the measuring geometry for low viscosity samples. We have also found that low stress values will result in very long equilibration periods for higher viscosity or viscoelastic systems. If the viscosity data is then plotted against solid phase volume fraction the resulting curve may be fitted to the Krieger-Dougherty equation using a suitable curve-fitting routine such as that supplied with Easy Plot [Cherwell Scientific Publishing Ltd, The Magdalen Centre, Oxford Science Park, Oxford OX4 4GA].

The values for intrinsic viscosity and ϕ_m are both obtained from this fitting procedure. We have found that samples having a wide range of ϕ values (ideally spanning ϕ_m) are required to obtain reliable values of intrinsic viscosity and ϕ_m with a minimum of extrapolation. We have found for the purpose of this fitting procedure that it is then best to exclude data where $\phi > \phi_m$ and solid-like behaviour dominates.

It should be noted here that attempts to measure MVPF by assessing aggregate structure by dibutyl phthalate (DBP) absorption do not correlate with the results obtained by the method described above and thus DBP absorption measurements cannot be employed as an indicator of MVPF.

It has been found that as the MVPF value of the solids content of the ink is reduced, the print quality is improved at a given concentration of the pigment, all other things being

equal. Preferably, therefore, the MVPF is not greater than 0.20 and more preferably not greater than O.15.

While there appears to be no uniformly direct relationship between MVPF and structure, in general high values of MVPF are associated with low structure and vice-versa. Thus, the observation that an increase in optical density of the printed dot obtained from a droplet of ink jet printer ink is obtained for a given concentration of a given pigment by reducing the maximum volume packing fraction is unexpected because it is contrary to the generally accepted teaching that colour density is enhanced by lowering structure or reducing particle size.

However, if the MVPF is too low, the viscosity of the ink may become greater than is desirable for printing at the concentration of pigment required to provide the desired depth of shade of colour. For this reason, it is preferred that the MVPF of the disperse phase is not less than about 0.05 to 0.06, preferably not less than 0.10, more preferably not less than 0.12.

In general, the greater the concentration of pigment having a given MVPF, the better the print quality; however increasing the concentration also increases the viscosity of the ink. Therefore the maximum concentration should not exceed 25% by weight. It has also been found that the viscosity of an ink containing a given concentration of pigment tends to increase with decrease in the value of MVPF of the disperse phase. Thus, on the whole, the maximum acceptable concentration of pigment in the ink tends to decrease with decrease in the value of MVPF. As a general guide, it has been found that where

carbon black forms the disperse phase, the concentration is preferably no greater than 25% by weight at an MVPF of 0.25 and the preferred maximum is about 11% at an MVPF of 0.05.

The optimum concentration of pigment in the ink will depend *inter alia* on its MVPF and its nature. It may also depend upon whether other insoluble solids such as extenders are present. In general, where it is the only component of the disperse phase it should be more than 7%. Nevertheless amounts less than 7%, e.g. down to 5%, or even as low as 2 or 3% for coated papers, may be acceptable, especially where the disperse phase includes other insoluble solids in addition to the pigment. However, it should not exceed 25%, preferably 20%, by weight of the ink. In many cases the concentration need not exceed 15%.

The value of intrinsic viscosity may also have some bearing on the performance of the ink in an ink jet printer. It seems that the intrinsic viscosity should desirably be at least 17 and perhaps preferably at least 20 but at significantly higher values, e.g. 100 or 110 and above, the ink may become difficult to use.

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

THE PIGMENT

The pigment is selected to be insoluble in the chosen diluent at ambient temperatures and also at the chosen operating temperature if that is above ambient temperature. Where it is

the only component of the disperse phase it should have an MVPF of not greater than 0.25, preferably less than 0.2, more preferably less than 0.15,. but in general greater than 0.05 to 0.06 and more preferably at least 0.10 or 0.12. Where the disperse phase contains other components, in addition to the pigment, then it is the MVPF of the entire disperse phase including these additional components which is relevant. Examples of such other insoluble components include extenders, e.g. clays, organo-clays and silicas.

In general the preferred pigments are found amongst those characterised as "pigment dyes" in the Colour Index. Mixtures of pigments may be used, if desired.

Preferably the pigment will be black or of a primary subtractive hue. It should also be lightfast, and thermally stable even with repeated warming. The pigment should be water insoluble to prevent smearing of the print upon contact with water-containing substances.

Carbon blacks having maximum volume packing fractions not greater than 0.25 and which are suitable for use in the invention are generally found amongst furnace blacks and other blacks formed by thermal-oxidative processes. Examples of suitable blacks are the furnace blacks Monarch 880 and Vulcan XC-72R from Cabot, acetylene black code 267 from Chevron and Continex N330 from Witco.

It will be understood that it is generally desirable for the specific gravities of the pigment and diluent, respectively, to be such that sedimentation of the pigment on storage of the ink is negligible.

THE DILUENT

The term "diluent", as used in this specification, refers to all components of the ink composition which, individually, are normally liquid at ambient temperatures. The diluent may be a single component or a mixture of such components.

While the diluent is preferably organic, it is believed that the invention is also applicable to aqueous inks. The diluent, whether a single component or a mixture, should be selected to form a low viscosity dispersion with the selected pigment, and other non-diluent components where employed. It is therefore desirable for the diluent itself to have a low viscosity. Ideally, the diluent viscosity at the operating temperature of the printer should not be more than 10 mPas, preferably not more than 6 mPas. Preferably the viscosity of the ink is less than 60 mPas and for ease of use in DOD printers, it is preferred that the viscosity of the ink be not more than 20 mPas, more preferably not more than 15 mPas. The viscosities referred to here are those measured at 30°C using a Bohlin CS rheometer with a CP 4/40 cone and plate geometry at a shear stress of at least 0.06Pa.

It is further preferred for the diluent to have a low volatility. In general it is preferred that the boiling point of the diluent be at least 100°C, more preferably more than 180°C, at atmospheric pressure. Where the diluent comprises more than one component, the reference to boiling point is to the temperature at which the mixture starts to boil.

While the surface tension of the diluent should not be too high because this could on the one hand retard diffusion into the paper fibres and on the other hand interfere with the

ejection of the ink from the nozzle in the preferred case where the ink is intended for use in a pressure wave actuated ink jet printer, the surface tension should not be too low because otherwise the separation of the drop ligament from the nozzle is impeded during drop ejection. Preferably, the surface tension should be in the range 20 to 40 mNm^{-1} at 25°C.

Organic diluents, especially polar organic diluents, are particularly preferred because they are also readily absorbable into cellulosic fibres, and therefore do not have to rely on volatility for removal from a dot printed on a paper substrate. Examples of polar organic solvents which are preferred are ethers of alkylene glycols and ethers of polyalkylene glycols. Specific examples include polypropylene glycol ethers and n-butyl ethers of ethylene glycol and polyethylene glycols, 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.

In one form, the diluent consists primarily or essentially of such a glycol ether or a mixture of such glycol ethers. However mixtures of these ethers with other diluents, especially organic diluents, are also contemplated.

Other diluents that may be employed include, for example, hydrocarbons, especially aliphatic hydrocarbons, and mixtures thereof with polar organic liquids e.g. esters, ethers, ketones, alcohols and mixtures thereof.

Thus, the diluents are preferably selected from hydrocarbons, organic polar diluents and mixtures thereof.

In one form of the invention, the diluent is preferred to be substantially non-aqueous, by which is meant that the diluent contains no more than about 5% by weight of water, including moisture absorbed from the atmosphere. In this embodiment, the diluent is preferably free of any added water and the amount of water it is capable of absorbing from the atmosphere under normal operating conditions (that is to say at ambient temperature and at the printing temperature, if other than ambient temperature) is no more than 2% and more preferably no more than 1%, by weight. An aqueous diluent is thus one which contains at least 5%, and preferably more than 50%, by weight of water.

RESINOUS DISPERSANT

A preferred embodiment of the ink of the invention includes a resinous dispersant for the pigment. The resinous dispersant, which may comprise a single component or a mixture of two or more components, should be selected to be capable in the absence of the pigment of dissolving in the chosen diluent at ambient temperature (and at the operating temperature of the print head if that is higher than ambient) and in the concentration in which it is employed in the ink, and to disperse the chosen pigment in the diluent so as to form a substantially stable dispersion. By "dissolve" we mean that the dispersant is in solution in the diluent or is so highly solvated by it that the product is substantially indistinguishable from a true solution under the conditions employed in ink jet printers in which it is employed. The dispersant preferably will also adhere well to a paper substrate since then it can also contribute to binding the pigment to the paper substrate.

Where the diluent is non aqueous, the resinous dispersant is preferably insoluble in water. Preferably it is chosen such that the combination of the dispersant and the chosen pigment will separate from the diluent when a droplet of the ink comes into contact with plain paper, e.g. due to action of the water in the paper and/or some other property or component of the paper, or because of the concentration effect caused by absorption of the diluent 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 diluent, when the solution is contacted with plain paper or with water. Thus, while the dispersant should be soluble in the chosen diluent and should also be soluble in mixtures of the diluent 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 diluent on addition of a larger concentration of water. Such water sensitivity reduces the risk of undesired spread of the dot.

Examples of suitable dispersants for non-aqueous systems are those sold by BYK Chemie GmbH of Germany under the trade names "ANTI-TERRA", "DISPERBYK" and "BYK", dispersants sold by Efka Chemicals BV of Holland under the tradename "EFKA" and dispersants sold by Zeneca under the tradename "SOLSPERSE" . It will be understood, however, that not all materials within the classes listed are necessarily dispersants for all combinations of pigments and diluent.

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

dispersant in the diluent is not greater than 20 mPas, and more preferably not greater than 10 mPas, when measured at 30°C and by the method and using the apparatus described hereinbefore for measuring viscosity.

It is to be understood that in the context of this invention the dispersant is neither part of the diluent nor part of the disperse phase as defined herein.

The ink may also contain other additives known to be employable in ink jet printer inks and which are capable of dissolving in the chosen diluent at ambient temperatures e.g. dispersion stabilisers, electrolytes, binders, surfactants, drag reducers and the like. Dissolved components, as well as dispersed solid particles, will have an effect upon rheological properties, and thus where the ink contains dissolved components such as a dispersant, it is preferred that the MVPF of the totality of non-diluent components of the ink, i.e. the dissolved components and the undissolved components, is not greater than 0.45 and preferably not greater than 0.4 when measured at 30°C.

This MVPF may be determined in the manner described above for the disperse phase but the volume fraction is now judged to be the sum of the non-diluent components of the ink.

PROPORTIONS OF INGREDIENTS

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

The amount of dispersant required will depend upon the choice of the diluent and the nature of the disperse phase and also the particle size of the disperse phase. If too little is used, the dispersion will be unstable. However, we have observed that there is a concentration of dispersant above which no further dispersive effect will be obtained. This level of concentration has been observed to correspond approximately to that at which the viscosity of the ink composition is a minimum and is usually slightly more than that concentration, e.g. up to about 10% more.. Nevertheless, in many cases, there appears to be no disadvantage in including the dispersant in an amount somewhat in excess of the level of concentration that yields the minimum viscosity, and indeed in some cases an improvement in print quality has been observed. The amount of dispersant that gives the minimum viscosity for a particular ink composition may be determined by measuring the viscosities of a number of compositions containing the dispersant in varying concentrations and plotting a graph of measured viscosity against concentration of dispersant.

The amount of dispersant required will depend upon the nature of the pigment and any other solids to be dispersed, the nature of the diluent and the nature of the dispersant itself but will generally be in the range of 0.1 to 1 part per part of disperse phase by weight although larger or smaller amounts may also be used. The weaker dispersants will normally have to be used in amounts lying in the upper part of the range, e.g. 0.5 to 1 part, whereas with the stronger ones, dispersion may be achieved with smaller concentrations, e.g. 0.1 to 0.6 part per part of disperse phase.

Preferably, the diluent forms at least 60% of the ink composition, more preferably 75% to 95% by weight. For most formulations, the diluent will form 80% to 90% by weight of the ink composition.

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 disperse phase and/or dispersant may be employed than in inks to be used at ambient temperature 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 in ink jet printers of ink compositions according to the invention containing simply the diluent, dispersant and pigment. In particular, the dot spread is lower and the colour density is higher, and in many cases, the strike-through is less than that normally obtainable with the same concentration of a pigment having a MVPF above 0.25.

Inks according to the invention may be prepared by any suitable process. In one method, dispersant and pigment are dispersed in a small amount of diluent, e.g. by milling, and

the resultant concentrated dispersion is then let down to the required concentration by addition of more diluent.

The invention is illustrated by the following Examples. In these Examples, carbon black is used as the pigment but it is expected that similar results will be obtained with other pigment colours.

Examples 1 to 5

In the following Examples:

TPM means tripropylene glycol monomethyl ether;

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

A number of ink samples were prepared using TPM as diluent, carbon black as pigment and EFKA 47EA as dispersant. The carbon concentration was varied keeping the dispersant-to-carbon ratio constant. This ratio varied with the choice of carbon black. Print was produced on Conqueror high white wove 100gsm paper from each ink sample using a piezo-electrically actuated drop-on-demand ink jet printer with a range of drop sizes and at 360 dpi (dots per inch). As the carbon concentration increased, the optical density of the print samples increased until either a plateau level was achieved or the concentration was so high that the ink was too viscous to print. The maximum optical density of print that could be obtained for each carbon is recorded in the Table below.

TABLE

Example No.	1[1]	2	3	4	5
Carbon black	A	B	C	D	E
Amount of EFKA 47 EA (g/g of carbon) [2]	0.4	0.6	0.8	0.7	0.8
Maximum volume packing fraction of carbon black	0.26	0.12	0.05	0.13	0.17
Intrinsic viscosity	16.6	48.0	109.1	17.6	21.2
Maximum volume packing fraction of all non-diluent components in ink [2]	0.48	0.30	0.15	0.30	0.39
Optical density of print[3]	1.19	1.35	1.27	1.37	1.36

(1) comparative

(2) assuming density of carbon black = 2.0 and density of dispersant = 1.0

(3) correct to ± 0.05.

where

A is Regal 250R of Cabot

B is Vulcan XC-72R of Cabot

C is Monarch 880 of Cabot

D is Acetylene Black 267 of Chevron

E is N330 of Witco

The significant improvement in optical density that is obtainable from inks when the MVPF of the pigment in the ink is less than 0.25 is readily seen.

While the MVPF of a pigment is an intrinsic property thereof, it is possible that the measured value may vary slightly depending on the medium employed for the measurements. It is therefore to be understood for the purposes of this invention that the MVPF values referred to therein are those obtained from measurements of pigment dispersions wherein the diluent is TPM, the dispersant is EFKA 47EA and the dispersant is employed in an amount of 10% in excess of that which gives the minimum viscosity for the composition.

Examples 6-9

A number of ink samples were prepared using the diluent, dispersant, pigment and ratio of dispersant to pigment employed in Examples 1, 2, 4 and 5 but in all cases using a pigment concentration of 10% by weight.

From each ink, print was produced on Conqueror high white wove 100gsm paper using a piezo-electrically actuated drop-on-demand ink jet printer with a range of drop sizes and at 360 dpi. The results were as follows:

Example No.	6[4]	7	8	9
Carbon Black	A	B	D	E
Optical Density of Print	1.18±0.05	1.35±0.05	1.31±0.05	1.30±0.05

[4] In this Comparative Example, the carbon black was used in an amount of 11% by weight.

CLAIMS

1. An ink jet printer ink composition which at ambient temperatures (15 to 30°C) is in the form of a dispersion having a disperse phase of finely divided solid in a diluent and containing pigment in the disperse phase and wherein the maximum volume packing fraction of the disperse phase is not greater than 0.25 at 30°C and, where the pigment forms the disperse phase, the disperse phase forms more than 7% but not more than 25% by weight of the ink .

2. A composition as claimed in claim 1 wherein the maximum volume packing fraction of the disperse phase is not greater than 0.2.

3. A composition as claimed in claim 1 or claim 2 wherein the maximum volume packing fraction of the disperse phase is not greater than 0.15.

4. A composition as claimed in any preceding claim wherein the maximum volume packing fraction of the disperse phase is greater than 0.05.

5. A composition as claimed in any preceding claim wherein the maximum volume packing fraction of the disperse phase is greater than 0.1

6. A composition as claimed in any one of claims 1 to 5 wherein the pigment forms the disperse phase.

7. A composition as claimed in any one of claims 1 to 5 wherein the disperse phase includes at least one insoluble component in addition to the pigment.

8. A composition as claimed in any preceding claim wherein the pigment is carbon black.

9. A composition as claimed in claim 8 wherein the carbon black is selected from furnace blacks and other blacks formed by thermal oxidative processes.

10. An ink jet printer ink composition which at ambient temperatures (15 to 30°C) is in the form of a dispersion having a disperse phase of finely divided solid in a diluent and containing pigment in the disperse phase and at least one component which is dissolvable in the diluent and wherein the overall maximum volume packing fraction of the components of the composition other than the diluent is not greater than 0.45 and the pigment is present in an amount of 7 to 25% by weight of the ink.

11. A composition as claimed in claim 10 wherein the maximum volume packing fraction of the components other than the diluent is not greater than 0.4.

12. A composition as claimed in claim 10 or claim 11 wherein said at least one component which is dissolvable in the diluent includes a resinous dispersant for the disperse phase.

13. A composition as claimed in any preceding claim wherein the diluent contains not more than the 5% by weight of water.

14. A composition as claimed in claim 13 wherein the diluent is organic.

15. A composition as claimed in claim 14 wherein the diluent is selected from hydrocarbons, polar organic liquids and mixtures thereof.

16. A composition as claimed in any one of Claims 13 to 15 including a dispersant which is soluble in the diluent and insoluble in water.

17. A composition as claimed in Claim 16 wherein the solution of dispersant in the diluent has a viscosity not greater than 20mPas at 30°C.

18. A composition as claimed in any preceding claim containing at least 60% diluent, by weight.

19. A composition as claimed in any preceding claim containing from 75 to 95% diluent, by weight.

20. A composition as claimed in any preceding claim containing a dispersant and wherein the dispersant is present in the composition in an amount which is equal to or greater than that at which the viscosity of the ink is a minimum.

21. A composition as claimed in any preceding claim which contains from 0.1 to 1 part of dispersant per part of disperse phase, by weight.

22. A composition as claimed in any preceding claim having an intrinsic viscosity at 30°C in the range 17 to 110.

23. An ink jet printer ink composition which at ambient temperatures (15 to 30°C) is in the form of a dispersion having a disperse phase of finely divided solid in a diluent and containing pigment in the disperse phase and wherein the maximum volume packing fraction of the disperse phase is not greater than 0.25 at 30°C and the intrinsic viscosity at 30°C is in the range 17 to 110.

24. A composition as claimed in claim 22 or claim 23 wherein the intrinsic viscosity is in the range 20 to 100.

INTERNATIONAL SEARCH REPORT

Internatic Application No
PCT/GB 95/02907

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D11/00

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 6 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 454 872 (SEIKO EPSON CORP) 6 November 1991 see page 3, line 49 - page 4, line 4 see page 5, line 17 - line 47 see page 6, line 13 - line 18 see page 7, line 41 - line 42; example 2.1 ---	1,6,8, 13-16, 22,23
X	WO,A,92 12209 (XAAR LTD.) 23 July 1992 cited in the application see page 11, paragraph 3 see page 12, paragraph 2 see page 13, paragraph 3 see page 14, paragraph 1 3 see page 17, paragraph 1 see page 21, line 1 - line 3 see page 22, paragraph 3 --- -/--	1,7-9, 13-16, 22,23

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"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

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"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
19 April 1996	15. 05. 96

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

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 408 333 (XAAR LTD.) 16 January 1991 cited in the application see page 4, line 24 - line 27 see page 5, line 32 - line 33 see abstract -----	1,7-9, 13-16, 22,23

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/GB 95/02907

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