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(54) **Ink additives for improved ink-jet performance.**

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EP 0 425 150 B1

Description

The present invention relates to inks used in ink-jet printers, and, more particularly, to an ink used in thermal ink-jet printers having improved kogation properties.

Thermal ink-jet printers offer a low cost, high quality, and comparatively noise-free option to other types of printers commonly used with computers. Such printers employ a resistor element in a chamber provided with an egress for ink to enter from a plenum. The plenum is connected to a reservoir for storing the ink. A plurality of such resistor elements are arranged in a particular pattern, called a primitive, in a printhead. Each resistor element is associated with a nozzle in a nozzle plate, through which ink is expelled toward a print medium. The entire assembly of printhead and reservoir comprise an ink-jet pen.

In operation, each resistor element is connected via a conductive trace to microprocessor, where current-carrying signals cause one or more selected elements to heat up. The heating creates a bubble of ink in the chamber, which is expelled through the nozzle toward the print medium. In this way, firing of a plurality of such resistor elements in a particular order in a given primitive forms alphanumeric characters, performs area-fill, and provides other print capabilities on the medium.

A problem with inks used in such thermal ink-jet printers is that the repeated heating of the resistor element over several hundreds of thousand or over millions of firings can cause breakdown of the ink, with consequent fouling of the surface of the resistor element. This process has been termed "kogation", which is defined as the build-up of residue (koga) on the resistor surface. The build-up of residue degrades pen performance.

Various ink compositions and processes have been developed in an effort to reduce kogation. For example, in the anionic dyes (sulfonate or carboxylate) commonly employed in aqueous inks used in thermal ink-jet printing, sodium is generally the counter-ion used. However, while dyes containing sodium counter-ions generally provide good print quality, sodium counter-ions have been found to contribute to the kogation problem.

One solution has been to partially or totally eliminate sodium. Successful replacement counter-ions are lithium and tetramethylammonium.

The need remains for the development of inks having reduced kogation, and hence longer life, using low cost chemicals with minimal additional processing.

DE-A-3132247 describes aqueous printer inks for ink-jet printers comprising a water-soluble dye, water and a surfactant phosphate ester. The presence of the surfactant phosphate ester is said to reduce clogging of the ink-jet nozzles.

The present invention provides an ink for thermal ink-jet printing comprising a vehicle consisting of at least one water-miscible organic compound and water, said vehicle having dissolved therein: from 1% to 12% by weight based on the weight of the ink of an anionic or cationic dye; and from 0.0009 to 14% by weight based on the weight of the ink of an oxo-anion selected from the group consisting of phosphate, diphosphate, monomethyl phosphate, dimethyl phosphate, arsenate, molybdate, sulfite and oxalate.

The addition of such oxo-anions essentially eliminates kogation for the life of ink pens, such as those used in Hewlett-Packard's DeskJet printer. Further, such oxo-anions will prevent kogation for inks containing dyes with negatively-charged water-solubilizing groups, such as sulfonate and carboxylate.

FIG. 1, on coordinates of weight (in nanograms, ng) and number of cycles (resistor firings), is a plot of drop weight versus cycles for three different energies of an ink not including the additive of the invention, depicting the effect of kogation on drop weight out to 5 million cycles; and

FIG. 2 is a plot similar to that of FIG. 1, but for an ink containing the additive of the invention, depicting essentially no kogation out to 10 million cycles.

Inks benefitted by the practice of the invention comprise a vehicle and a dye. The vehicle comprises one or more water-miscible organic compounds, such as a glycol or glycol ether and water. The dye may be any of the anionic or cationic dyes. The dye is present in an amount ranging from 1 to 12% (by weight), although more or less dye may be used, depending on the vehicle/dye system, the desired optical density, etc. Typically, the dye concentration is 2 to 6% (by weight). All amounts herein are by weight, unless otherwise indicated.

Particularly employed as inks herein are ICI dyes 286 and 287, preferably in a 50-50 mixture. However, any of the well-known dyes may alternately be used.

The particular water-miscible organic compounds and their concentrations does not form a part of this invention. However, examples of such compounds include glycols such as ethylene glycol, diethylene glycol, propylene glycol, polyethylene glycol, etc., and pyrrolidones, such as 2-pyrrolidone. Usually, the glycol is present in an amount up to 50%, and more typically up to 10%, with the balance water. The pyrrolidone is usually present in an amount of 7 to 10%, with the balance water.

Other additives may be added to the ink, such as fungicides, bactericides, pH adjusters, and the like, as is well-known. Such additives, and the materials comprising the vehicle and dye are of a purity commonly found in normal commercial practice.

In accordance with the invention, the addition of a compound containing an oxo anion significantly reduces kogation, and may even eliminate it entirely. Examples of such oxo anions include phosphates (both PO_4^{3-} and $P_2O_7^{4-}$) and monomethyl or dimethyl phosphate esters. Further examples of oxo anions beneficially employed in the practice of the invention include, in descending order of preference, arsenate (AsO_4^{3-}), molybdate ($Mo_7O_{24}^{6-}$), sulfite (SO_3^{2-}), and oxalate ($C_2O_4^{2-}$). Anions other than these may not have a beneficial effect. For example, nitrate and thiocyanate anions are ineffective with the ICI dyes mentioned above. As used herein, an oxo anion is a class of anions in which various elements are bound to oxy-gen and which bear an overall negative charge in aqueous solution.

The most effective additive to date are phosphate salts; added either as dibasic (HPO_4^{2-}), monobasic ($H_2PO_4^{2-}$), polyphosphates such as diphosphate ($P_2O_7^{4-}$), or monomethyl or dimethyl phosphate esters.

The phosphate species in solution is determined by the pH of the ink. In the pH range of 8 to 9 (typical for inks containing ICI dyes), the predominate species for both mono and dibasic phosphate is HPO_4^{2-}.

FIG. 1 depicts a measure of kogation from an ink comprising a vehicle of 10% 2-pyrrolidone and 0.2% sodium borate, the balance water, and 2.2% of a 50-50 mixture of ICI 286/287 dyes (NH_4^+ form). The pH was adjusted to 8.5 with NH_4OH. In this ink, no additive was used, and it is clear that there is a large decrease in drop volume (determination is by weight) with this ink, beginning almost immediately.

For comparison, kogation results for the same base ink composition with 0.1 wt% ammonium phosphate are depicted in FIG. 2. The addition of ammonium phosphate clearly yields an ink with constant drop volume. This ink evidences substantially flat behavior even out to 30 million cycles.

The selection of the counter-ion is not critical, other than it not adversely interfere with the reduction in kogation. Examples of suitable cations include alkali metals, ammonium, and alkyl ammonium. An especially efficacious compound is ammonium phosphate. Phosphate ion can also be added as phosphoric acid (H_3PO_4), along with neutralization with an appropriate base.

The concentration of the kogation-reducing additive (anions) of the invention ranges from 0.0009 to 14 wt%, based on the oxo anion. Less than 0.0009 wt%, while effective, is not enough to yield stable drop volumes out to several million firings. Greater than 14 wt% provides no further benefit. Preferably, the concentration of the oxo anion ranges from 0.01 to 1 wt%.

As indicated earlier, kogation degrades pen performance. A decrease in pen performance can be monitored by measuring (weighing) drops fired from a pen. A change in drop volume indicates the formation of resistor residues.

Without subscribing to any particular theory, it appears that the kogation effect is due to adsorption of dye and/or decomposition products of ink on the resistor surface. The appearance and increase in adsorbed dye or decomposition products apparently reduces the volume of ink fired. The additive of the invention is believed to eliminate or reduce the adsorption process.

The addition of ammonium phosphate to inks at relatively low concentrations (0.02 to 0.5%) yields inks which have constant drop volumes out to many million drops. For example, inks containing such amounts of ammonium phosphate have shown that ink volumes remain constant to at least 30 million drops. The same inks without ammonium phosphate do not have constant drop volumes, as indicated earlier with reference to FIGS. 1 and 2.

Examination of the resistors from inks without and with the addition of ammonium phosphate shows that there is a large amount of residue (koga) on resistors for inks without phosphate fired only to 5 million cycles and essentially clean resistor surfaces for inks containing phosphate when fired twice that number of cycles (10 million).

Auger Electron Spectroscopy has determined that the resistor residue primarily comprises carbon. Other elements, such as nitrogen, oxygen, and sulfur are at relatively lower concentrations. The resistor surfaces exposed to non-phosphate containing inks have a thick carbon layer (corresponding to adsorbed dye) and/or ink decomposition products, whereas the resistor surfaces exposed to phosphate-containing inks have only a very thin carbon layer, together with some phosphorus. Apparently, phosphate is being adsorbed on the resistor surface, and prevents the adsorption of dye and/or ink decomposition products thereon.

Interestingly, the foregoing suggests that the process of kogation is reversible. Indeed, pens have been kogated by firing with an ink that does not contain phosphate to several million cycles until the drop volumes decrease considerably. Refilling these pens with a phosphate-containing ink yields complete recovery of the pen. That is, the drop volumes rise to a "normal level" of about 140 pℓ.

The pH of the inks is adjusted to be within the range of about 3 to 10, and preferably about 8 to 9

for the ICI dye examples discussed herein, using commonly-employed pH adjusters.

Example 1:

In this example, the preparation of an ink containing phosphate is described.

The ink comprised a vehicle of 10% 2-pyrrolidone, 0.2% sodium borate as a pH buffer, and the balance deionized water and 2.2% of 50-50 ICI 287/287 dye. Monobasic ammonium phosphate ($NH_4H_2PO_4$) was added to the foregoing ink to provide a concentration of 0.1 wt% therein. The initial pH was adjusted to 8.5 with concentrated NH_4OH.

Example 2:

The ink from Example 1 was tested for kogation out to 10 million cycles. The parameter which has been used to evaluate the effectiveness of an additive is drop volume. In this test, droplets ejected from a pen are collected and weighed in a pan on an analytical balance. An average weight is obtained and is commonly referred to as drop volume in picoliters (pℓ). The current test operates at three different energies (15%, 30%, and 45%) over that required to fire a droplet from a nozzle in order to obtain a range of performance (OE). In a given printer and a given pen under normal operating conditions, a pen will be operating at a single energy.

The results are depicted in FIG. 2, as discussed above. In FIG. 2 (and in FIG. 1), the dashed line represents 15% OE, the heavy solid line represents 30% OE, and the light solid line represents 45% OE.

Example 3:

For comparison, the same ink as in Example 1 was prepared, but omitting the ammonium phosphate. The ink was tested as in Example 2. The results are depicted in FIG. 1, as discussed above.

Clearly, the ink without ammonium phosphate is seen to exhibit kogation within a very short number of cycles, while the ink containing ammonium phosphate is stable against kogation out to at least 10 million cycles.

Example 4:

A mixture of dimethyl phosphate (55%) and monomethyl phosphate (45%) was added to an ink which was the same as in Example 3, except that the amount of pyrrolidone in the vehicle was 7.5%. The total phosphate ester concentration was 0.5 wt% and the pH of the ink was adjusted to 8.5. This ink had stable drop volumes when tested to 4.8 million cycles.

Example 5:

Addition of 0.2% ammonium phosphate to an ink prepared with the sodium form of Direct Black 168 (1.9 wt%) in a vehicle of 5.5% diethylene glycol, balance water, yielded excellent results. The drop volumes were constant when tested to 9 million cycles.

Example 6:

Addition of 0.5% of a mixture of dimethyl phosphate (55%) and monomethyl phosphate (45%) to an ink prepared with the lithium form of Acid Red 27 (3 wt%), a magenta dye, in a vehicle of 5.5 wt% diethylene glycol, balance water, yielded stable drop volumes for all energies when tested to 4.8 million cycles.

Example 7:

Addition of 0.2% ammonium phosphate to an ink prepared with Acid Red 27 (3 wt%) in a vehicle of 5.5 wt% diethylene glycol, balance water, yielded stable drop volumes for all energies for all energies (15%, 30%, 45% OE) after an initial rise, which converged at approximately 160 pℓ. Each OE curve rose at a different rate and was stable after 0.4 million for 45% OE, 1.4 million for 30% OE, and approximately 3 million for 15% OE. This demonstrates that after some initial "break-in period", phosphate stabilized the drop volumes at a high level, giving excellent results.

Thus, there has been disclosed an additive for reducing or eliminating kogation in inks used in thermal ink-jet printers. It will be readily apparent to those skilled in this art that various changes and modifications may be made within the scope of the invention as defined by the appended claims.

Claims

1. An ink for thermal ink-jet printing comprising a vehicle consisting of at least one water-miscible organic compound and water, said vehicle having dissolved therein:

   from 1% to 12% by weight based on the weight of the ink of an anionic or cationic dye; and

   from 0.0009 to 14% by weight based on the weight of the ink of an oxo-anion selected from the group consisting of phosphate, diphosphate, monomethyl phosphate, dimethyl phosphate, arsenate, molybdate, sulfite and oxalate.

2. An ink according to claim 1 wherein said vehicle comprises at least one glycol and the balance water.

3. An ink according to claim 1 or 2 wherein said vehicle comprises up to 10% by weight of diethylene glycol and the balance water.

4. An ink according to claim 1 wherein said vehicle comprises at least one pyrrolidone and water.

5. An ink according to claim 4 wherein said vehicle comprises up to about 10% by weight of 2-pyrrolidone and the balance water.

6. An ink according to any preceding claim wherein the oxo-anion is selected from the group consisting of phosphate and diphosphate.

7. An ink according to any preceding claim wherein the oxo-anion is present in an amount of from 0.01 to 1% by weight based on the weight of the ink.

8. A method of reducing kogation in a thermal ink-jet printer comprising the step of printing with said printer using an ink according to any of claims 1 to 7.

Patentansprüche

1. Eine Tinte zum thermischen Tintenstrahldrukken, die ein Lösungsmittel aufweist, das aus zumindest einer wassermischbaren organischen Verbindung und Wasser besteht, wobei folgende Stoffe in dem Lösungsmittel aufgelöst sind:
von 1% bis 12% Masseanteil eines anionischen oder kationischen Farbstoffes, basierend auf dem Gewicht der Tinte; und
von 0,0009 bis 14% Masseanteil eines Oxo-Anions, basierend auf dem Gewicht der Tinte, das aus der Gruppe ausgewählt ist, die aus Phosphat, Diphosphat, Monomethyl-Phosphat, Dimethyl-Phosphat, Arsenat, Molybdat, Sulfid und Oxalat besteht.

2. Eine Tinte gemäß Anspruch 1, bei der das Lösungsmittel zumindest ein Glykol und als Rest Wasser aufweist.

3. Eine Tinte gemäß Anspruch 1 oder 2, bei der Lösungsmittel bis zu 10% Masseanteil an Diethylen-Glykol und als Rest Wasser aufweist.

4. Eine Tinte gemäß Anspruch 1, bei der das Lösungsmittel zumindest ein Pyrrolidon und Wasser aufweist.

5. Eine Tinte gemäß Anspruch 4, bei der das Lösungsmittel bis zu etwa 10% Masseanteil von 2-Pyrrolidon und als Rest Wasser aufweist.

6. Eine Tinte gemäß einem beliebigen vorhergehenden Anspruch, bei der das Oxo-Anion aus der Gruppe, die aus Phosphat und Diphosphat besteht, ausgewählt ist.

7. Eine Tinte gemäß einem beliebigen vorhergehenden Anspruch, bei der das Oxo-Anion in einer Menge von 0,01 bis 1% Masseanteil, basierend auf dem Gewicht der Tinte, vorliegt.

8. Ein Verfahren zum Reduzieren der Kogation in einem thermischen Tintenstrahldrucker, das den Schritt des Druckens mit dem Drucker unter Verwendung einer Tinte gemäß einem beliebigen der Ansprüche 1 bis 7 aufweist.

Revendications

1. Encre pour impression thermique à jet d'encre, comprenant un véhicule constitué d'au moins un composé organique miscible avec l'eau et d'eau, ledit véhicule comportant, en solution:
de 1% à 12% en poids, par rapport au poids de l'encre, d'un colorant anionique ou cationique; et
de 0,0009 à 14% en poids, par rapport au poids de l'encre, d'un oxanion choisi dans le groupe constitué par le phosphate, le diphosphate, le phosphate de monométhyle, le phosphate de diméthyle, l'arséniate, le molybdate, le sulfite et l'oxalate.

2. Encre selon la revendication 1, dans laquelle ledit véhicule comprend au moins un glycol, le reste étant de l'eau.

3. Encre selon la revendication 1 ou 2, dans laquelle ledit véhicule comprend jusqu'à 10% en poids de diéthylèneglycol, le reste étant de l'eau.

4. Encre selon la revendication 1, dans laquelle ledit véhicule comprend au moins une pyrrolidone et de l'eau.

5. Encre selon la revendication 4, dans laquelle ledit véhicule comprend jusqu'à environ 10% en poids de 2-pyrrolidone, le reste étant de l'eau.

6. Encre selon l'une quelconque des revendications précédentes, dans laquelle l'oxanion est choisi dans le groupe constitué par le phosphate et le diphosphate.

7. Encre selon l'une quelconque des revendications précédentes, dans laquelle l'oxanion est présent dans une proportion de 0,01 à 1% en poids, par rapport au poids de l'encre.

8. Procédé de réduction de la kogation dans une imprimante thermique à jet d'encre, comprenant l'étape d'impression avec ladite imprimante à l'aide d'une encre selon l'une quelconque des revendications 1 à 7.

Fig. 1. (Prior art)

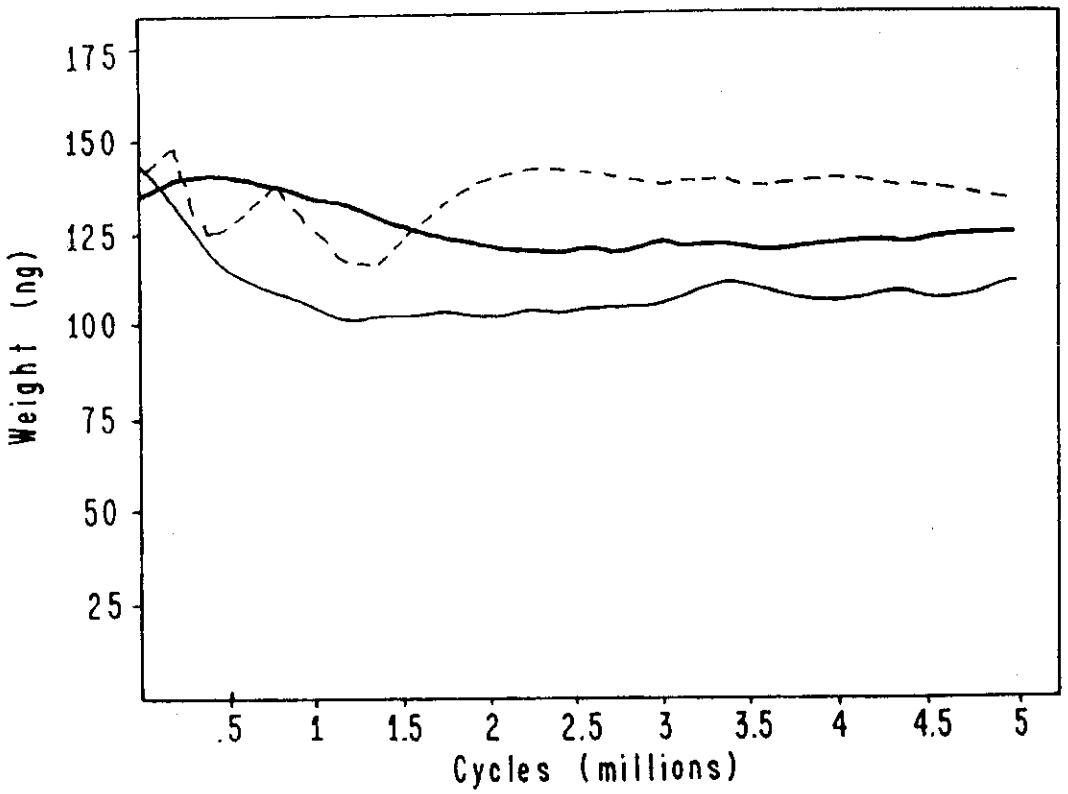
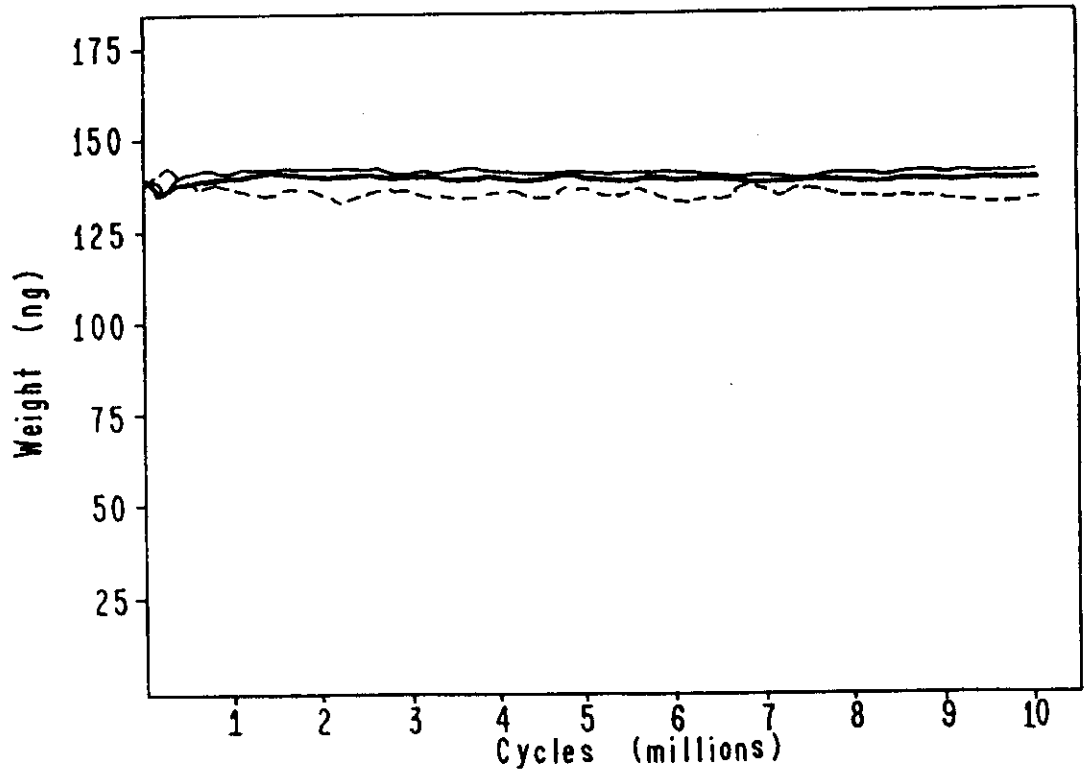


Fig. 2.



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