
Materials Aspects for High Quality Color Thermal Ink Jet Printing

P. Gendler

IBM Research Division, Almaden Research Center, San Jose, California

Introduction

Historically, the potential performance advantages of ink jet printing, which made it such an attractive technology, have included low cost, good print quality (PQ), and quiet operation not available in other printing processes. The awareness of these, and other, potential advantages has resulted in a great deal of effort in developing ink jet technology to the state where many commercial printers of several types are now available. The present discussion will explore those chemical/material properties of ink jet inks which influence much of the technology and control the performance.

The discussion will be limited to those most recent developments in the patent literature, approximately covering the period from 1989 through 1992. The information is divided into the two main topics of 'chemistry of dyes,' and 'chemistry of carriers (or solvents),' with a few subtopics.

General Ink Requirements

Regardless of the exact ink jet application, that is for continuous ink jet, piezoelectric tube drop-on-demand, or thermal drop-on-demand, all ink jet inks must satisfy certain requirements: safety/toxicity, performance

(including reliability, low maintenance, long lifetime), print quality (including fast drying, no bleeding or print-through, smear resistance, waterfastness, and lightfastness).

As is the case with many technologies, ink jet has the problems of very complex interactions between ink components and their effects on performance. Adding the wrong dye, or buffer, or as little as 0.1% of the wrong biocide, can cause profound problems with kogation, or reliability. Kogation is unique to thermal ink jet and is caused by the thermal decomposition of organic matter and subsequent deposition of the products of decomposition on top of the heater; the deposit can thermally insulate the heaters and cause retarded jet velocity, misplaced drops, and more. Some of the ink requirements are difficult to achieve and result in narrow regions of acceptable concentrations of ink components, such as the desire that the ink should be stable in the printer, but dry quickly on contact with the substrate. Accordingly, the ink chemist needs to be aware of and be able to convey to others interested in the technology the trade-offs that have to be considered.

1989-1992 Ink Jet Materials Patents Overall Statistics

During the three year period from 1989 to late 1992 there were 382 ink jet patents dealing *only* with materials. This does not include any patents dealing with substrates, packaging, or the myriad other aspects of the technology that received coverage. Of these materials patents 88 dealt specifically with colorants. Also specifi-

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cally covered were solvents/carriers, both dyes/carriers, and other materials related aspects like reliability, fastness, corrosion, dry time, print quality, or kogation. These patents arose from the work of 41 different assignees, and occupied 260 different authors. There were 159 JP issues and 81 US issues. Of the 81 US issues 31 were assigned to Hewlett Packard, 27 to Canon and 10 to Xerox; the US issues had 150 different authors.

Dyes: Waterfastness

The main concerns with dyes for ink jet are their effect on maintenance, their color, fastness to water and light; also of concern is safety and to a lesser extent cost. Since previous work has explored the constraints of dye/ink purity on maintenance, the effect of the cation on maintenance [although there is still some recent work in the area (US 4994110, US 4994111)], and since the safety of all new chemicals for use in home or office must be routinely assured, and the relatively low amount of dye required in an ink makes cost not a huge issue, the waterfastness topic will be explored here.

A difficult problem is the desire to have water-soluble dyes that have waterfastness after contact with the substrate. However, several approaches were adopted, not including ways involving special substrates or two step printing. Various dyes were prepared with substituents which were intended to anchor the dyes to the substrate, in this case 'plain paper.' Thus the need is for a water-solubilizing group that might have affinity for paper, i.e. cellulose. One such substituent is amines, both mono- and poly-functional, which form dyes with positive charges, so-called 'cationic dyes,' instead of the usual negatively charged anionic dyes. Cationic dyes have much higher waterfastness than typical anionic dyes due to increased interaction with the substrate and are covered in DE 3739456, EP 335237, US 5019165, US 5026425, US 5098475, US 5106416. Others suggest the use of separate cationic species to bind the dye to the substrate like poly-amines (US 5129948). Another such substituent with cellulose affinity is the boronic acid (B(OH)₂) which is known to have high affinity for alcohols, such as found in cellulose (US 5108502). Another method is to enclose the dye in a matrix that does not interfere with the color or any other dye requirement, and has affinity for cellulose such as the center of a cyclodextrin (US 4836851, US 4838938, US 5108505); cyclodextrin is a cyclic sugar of six to eight repeating units, and resembles cellulose, a polymer of sugar molecules. Another method is to bind the dye to a matrix, contain it in or bind it to a micelle (DE 4211262, US 5106416, US 5108504, US 5116409, US 5145518), or bind it to a polymer (JP 91250069, EP 465124), and have the bound dye be attracted to the cellulose. Other work involved the use of various substituent poly-hydroxy bearing dyes (US 4836851), where the poly-hydroxy groups resemble cellulose and can be aimed at both better dye solubility (reliability) and waterfastness. Still other work involves the use of reactive dyes which form covalent bonds with the substrate on heating or on standing (EP 366121); while some prefer to specifically eliminate reactive dyes (US 5118737).

An effective way to achieve waterfastness in a water soluble dye is to replace the typical water solubilizing group found in dyes, the sulfonate (SO₃⁻), with the carboxylate (CO₂⁻), as covered in US 4963189, US 5053495, EP 468649, and EP 494522. The key to the success is the relative acidity of the two groups, and relies on the fact that dyes with a CO₂⁻ will become insoluble on contact with the substrate.

Carriers: Substrate Independence

The subject of solvents/carriers for high quality thermal ink jet printing can be further divided into liquid and solid (the so-called 'hot-melt') systems, and both can be aqueous or non-aqueous systems. A few representative liquid and hot-melt systems will be mentioned. The parameters that the ink chemist must juggle and the corresponding ink properties are difficult to balance and this results in narrow acceptable concentration ranges. In fact if they are viewed as if these parameters and properties are found on corners of a triangle, that seems to approach the true situation. The corners can be considered to be occupied by print quality, dry time, and maintenance. This 'infernal triangle' may indicate that maximizing one property might result in problems with one or both of the others. For instance, additions of surfactants and/or penetrants to an aqueous ink will, by lowering the surface tension, reduce the dry time to values of less than a second. The smear resistance will be greatly improved but in our experience the print quality that results is poor because the ink flows along the paper fibers and gives a ragged edge to the print ('feathering'). If the colorant used is a pigment, an insoluble dye (or, for that matter, if any other insoluble solid is present) in an attempt to get fastness, the reliability can be compromised due to the precipitation of the particles in the nozzles, and the kogation (lifetime) is adversely affected. There are numerous items dealing with pigments (US 4749506, US 5106407, US 5123959, US 5125968, US 5145518, US 5160372, US 5169436, US 5169438).

Liquid Carriers

The changes in the past three years to the liquid carriers have involved many iterations of a similar story: depending on the specific application, the use of every conceivable type of water miscible chemical has been covered. There are a legion of patents citing use of familiar, low MW, water soluble organic compounds like the glycols, glycol ethers, amides, ureas, sulfonamides, sulfoxides, and sulfones, etc., and combinations thereof. Some of the novel approaches are the use of carboxamides (R1CONHR2, US 5131949), cyclic aliphatic diols used specifically for pigment dispersions (US 5169438), and tris-(hydroxyalkyl-ethers) of glycerol (HOCH₂CHOHCH₂OH) (US 5169437), which also are claimed to reduce kogation.

The use of micelles, suspensions, or emulsions has been suggested numerous times as noted above (DE 4211262, US 5106416, US 5108504, US 5116409, US 5145518). The usual problem with suspensions or emulsions is one of phase separation or instability. An emulsion is a meta-stable situation and can not reform

spontaneously once it is broken up by an outside energy source like a freeze-thaw cycle. An emulsion requires the input of a great deal of energy to be formed from its components, like high speed, high shear mixing. A suspension is also meta-stable and the particles tend to agglomerate forming larger particles which eventually interfere with performance.

A remedy for the instability of emulsions was the microemulsion, a thermodynamically stable arrangement of a mixture of polar and non-polar chemicals, related to the classic emulsion but very different. The problem with typical emulsions of instability to freeze-thaw was considered prohibitive and the advantage that a microemulsion has is its stability, since the microemulsion is thermodynamically stable and forms spontaneously. In fact microemulsion inks are stable to freeze-thaw cycles (US 4409039, US 4749506).

Solid Carriers

The patented solid hot-melt systems that form solutions at the elevated operating temperature of the head are composed of a laundry list of low MW, organic compounds which have melting points from near ambient to a few hundred degrees centigrade. Many of the patents cite useful operating ranges of the resulting mixtures at about 75°C. Inks derived from these compounds are covered in US 4878946, 5006170, 5102460, 5118347, 5122187, 5151120, and 5164232 and cover such varied compounds as esters, amides, sulfonamides, and phosphates.

A further refinement and extension of the microemulsion is to formulate them to be solids at ambient temperature. This results in a 'hot-melt' ink and it has appeared (US 5047084). A related area is that of the sol-gel hot-melt inks which also has appeared (US 5021802). The latter document notes that the gelling agent, like carrageenan, needs to be controlled between 0.25% and 0.50% by weight for viscosity reasons which is a narrow operating range. The use of carrageenan and related gelling agents at similar concentrations and with specific surfactants is covered in US 5108504.

Conclusions

The large number of materials related patents resulting from the work of a large number of inventors during the brief three year period of 1989-1992 reveals that a great deal of effort has been placed on the importance of materials to ink jet printing. Several attempts have been made to produce waterfast yet water soluble dyes, and the goal of substrate independent carriers has been approached by modifications to liquid aqueous and non-aqueous systems, and by the use of solid hot-melt systems. In all cases, the knowledge of the trade-offs between the ink properties and the desired performance is critical.

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