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Development and Characterization of Ink for an Electrostatic Ink Jet Printer

Abstract: This paper reviews the development of the ink for an electrostatic ink jet printer. It discusses the formulation logic, test procedures, failure analyses, and problem resolutions. The variables that influence the jet printing process and print quality are defined, and their relationship to specific formulations is discussed. Also considered are the relationships between formulation variables and failure modes inherent in the ink.

Introduction

An ink for use in an electrostatic ink jet printer must meet two distinct sets of requirements. The first is related to quality in the printed document: The image must be sharp, dense, and permanent. The second set is defined by the printer environment: The ink must be chemically stable and compatible with the materials that it contacts, and it must have physical properties suitable for jet formation and charging (see Table 1).

This paper reviews the technical problems encountered in developing a jet printer ink, and it discusses the formulation logic, test procedures, failure analyses, and problem resolutions. The variables that influence the jet printing process and print quality are defined, and their relationship to specific formulations is discussed. The dependence of failure modes inherent in the ink itself, such as solution instability, biological growth, and the effect of unsatisfactory stream dynamics on the formulation variables, is also discussed.

Complex interactions between inks and machine components are examined. It is shown that ink constituents must be selected to ensure compatibility with mechanical components and to resolve such system problems as deposits in the nozzle orifice, ink drying during machine shutdown, and evaporation of the vehicle during recycling.

Ink formulation

• *Vehicle selection*

Inks are composed of a colorant and a vehicle for the colorant, with additives to achieve desired functional objectives. Vehicles for liquid inks previously formulated in this laboratory for typewriter ribbons have been nonvolatile and water insoluble (i.e., mineral oil, oleic acid). However, these materials are not satisfactory for jet printer ink because of their high viscosity and nonionic character, which limits their conductivity. Although no fluid meets all the requirements for jet printer inks, we chose water as the vehicle because of its low viscosity, small viscosity change with temperature, and potential to be made conductive for proper drop charging. We found two disadvantages to a water vehicle: It is an ideal medium for biological growth and corrosion, and the drops traveling through the air incur evaporative losses. Methods to manage these disadvantages have been developed and are addressed in this paper and in [1].

• *Colorant selection*

The colorant chosen for the ink jet printer also deviates from what has been used in liquid inks for typewriter ribbons; namely, carbon black. Carbon black is a pigment, existing as discrete particles dispersed in the vehicle. Because of the small nozzle diameters and filter pore sizes, and also because of the potential long-term stability problems with particulates, we felt that an ink with a water-soluble dye had a greater probability of success than a pigmented one.

The use of a water-soluble dye raises questions concerning the optical density and water fastness of the print. Optical density is limited by the solubility of the dye and by its absorbance, and water fastness is clearly an exposure in a water-soluble system. However, certain dyes are used commercially for coloring textiles and paper in applications with these requirements, and several such black dyes were selected as candidates. These

Table 1 Ink requirements.

Chemical stability	
Shelf life	18 months
Physical properties	
Viscosity	1-5 $\mu m^2/s$; minimum change with temperature and concentration
Resistivity	<1000 Ω-cm
Stream properties	
Stability	Free from "jitter"
Print window	Satellite-free stream at operating point
Reliability	
Nozzle clogging	None
Filter clogging	1 year life
Nozzle crusting	>2 weeks
Ink-parts interaction	No solvent action; no corrosion
Output	
Print quality	Optical density >1.0
Drying time	<10 s
Archival properties	Fade-ometer 72 h Water 48 h
Environmental	
Toxicity	Nontoxic
Flammability	Nonflammable

commercial dyes typically contain impurities from the synthesis process and additives appropriate to their usual application; however, we felt that purification of these dyes or synthesis of a dye for this application alone would be unattractive alternatives because of the excessive cost.

To choose a dye that would meet our requirements for optical density, a screening program was conducted (Table 2). Optical densities of dyes were compared by calculating the absorption coefficient a at the maximum wavelength λ of an absorption spectrum in the visible region (350 nm to 700 nm).

The absorption coefficient was determined for several commercially available black dyes. The dyes numbered 4 and 8 in Table 2 appeared to be the best choices.

The dye chosen also alleviated the problem of water fastness of print, since it has an affinity for cellulose that renders it resistant to removal with water. In addition the preferred dye reduces exposure to corrosion, since it is soluble in the pH range of 9 to 11. (This range corresponds to the region of minimum corrosivity for stainless steel in aqueous fluids containing chloride ions [2].)

Because of the complexity of the synthesis scheme, many side products and intermediates may appear in the final product. Additives may also be present. Table 3 gives the results of chemical analysis of a typical commercial dye. Components in the commercial product, other than dye, can be classified according to the following scheme:

Inorganic Sodium chloride is present as a diluent and as a by-product of adding hydrochloric acid to precipitate the dye from solution after synthesis. Sodium carbonate is added to adjust the pH for maximum dye solubility.
Nonpolar organic Dedusting agents are added to the dye after it has been dried. Mineral oils and phthalate plasticizers are typically used.
Polar aromatic These are nonsulfonated side products of the synthesis; i.e., chrysoidine, Bismark Brown, and any unreacted starting materials.
Trace metals Trace metals found in the dye come primarily from the water used in the synthesis reaction.

For optimum performance in an ink jet system and for long-term stability, the nonpolar organic, polar aromatic, and trace metal content of the dye had to be kept low. The levels shown in Table 3 were found to be acceptable.

• *Additives*

Many of the requirements for jet printer ink are met by a solution of a black dye in water; such an ink, which can be used for jet printing, produces satisfactory print quality and archival properties. Indeed, the first jet printing was accomplished with a commercial fountain pen ink [3]. However, several problems exist with such a simple system, and many of these must be solved with additives.

Nozzle crusting

A problem familiar to users of drafting pens or fountain pens is crusting; when a pen is left uncapped, ink dries in the nib, producing a crust that prevents the normal flow of ink. A similar phenomenon occurs in the ink jet nozzle, resulting in stoppage or deflection of the jet after stream shutdowns of an hour or so. Dye dries from solution to produce a hard, crystalline crust that is not easily removed by the pressure used to propel the stream. Because capping the nozzle is not possible due to the small clearance between it and the charge electrode, a solution through formulation was required. A screening program was instituted to find a material compatible with the ink and effective at levels that do not greatly increase viscosity. The material selected prevents crusting after shutdown periods of two weeks or more.

Nozzle clogging

The small orifice required for stream formation in ink jet printing is easily clogged by small particles carried in the ink. The diameter of this orifice corresponds closely to that of paper fibers and dust from various sources. Since

most of the ink passing through the orifice is recirculated up to forty times, there is ample opportunity for contamination by airborne particles. The system must therefore be provided with filters to protect various components from particulate contamination and especially to prevent particles from reaching the nozzle and clogging it.

We chose depth filters, rather than surface filters, as the primary filtration medium, since continuous contamination is known to occur and the filter accumulates a considerable quantity of contamination during the life of the printer. In addition, a screen and a prefilter are included in the ink circulation system between the source of contamination and the primary filter [1].

Even with these filters in place, nozzle clogs were occasionally observed in development models. At first, dye agglomeration or biological growth in ink was suspected. However, direct examination of these minute clogs by x-ray analysis of scanning electron microscope signals showed them to be of two types: those containing silicon and those made up of metals. We attributed the former to dust, the latter to manufacturing artifacts – materials left in the system during machining and assembly. Both were eliminated by adding a small surface filter as near to the nozzle as possible, in the printhead itself.

While an additive was not directly involved in the solution to this problem, it may be seen from the next discussion that the use of filters led indirectly to the incorporation of additives to prevent filter clogging.

Filter clogging

The filters used to protect against nozzle clogs are themselves subject to clogging by particles of a size roughly equal to their pore size, especially by gelatinous substances. The size and quantity of particles entering the ink circulation system through the gutter are not likely to clog filters. But the generation of particles in the ink by chemical or biological action poses a serious threat and had to be prevented with ink additives.

To ensure that an ink under consideration did not have an inherent tendency to clog filters, a flow test was devised. The test is conducted by monitoring the flow rate of ink through a filter for ten minutes at constant pressure. Specifically, the flow rate is monitored at one-minute intervals as the ink flows through a 5-μm Teflon® [4] surface filter at 5 psi. The change in flow rate is a better measure of ink performance than the total flow because of the variations among filters. However, very low values of total flow indicate a high pressure drop across the filter. Good performance is indicated by a steady or increasing flow rate (an increase is due to wetting of the filter); a decreasing flow rate indicates filter clogging.

We observed filter clogging due to dye solution instability. Dye solubility is reduced at pH values below 9.0.

Table 2 Black dye screening program.

Dye	λ_{max} (*nm*)	*a**	λ_{max} (*nm*)	*a**
Sample 1	488	18.9	575	17.7
Sample 2	574	13.0	–	–
Sample 3	565	14.9	–	–
Sample 4	491	28.5	606	31.2
Sample 5	520	11.4	659	15.4
Sample 6	490	10.5	590	11.0
Sample 7	609	31.7	465	17.1
Sample 8	488	28.8	606	29.2
Sample 9	566	20.5	–	–
Sample 10	600	19.8	–	–

*Absorption coefficient

Table 3 Typical commercial black dye composition.

Dye	68%
Inorganic	
Sodium chloride	26%
Sodium carbonate	4%
Nonpolar organic	
Deduster	0.2%
Polar aromatic	
Reaction side products	1.0%
Trace metals	
Iron	385 ppm
Copper	38
Calcium	415
Lead	<100
Aluminum	<100
Magnesium	<100
Silicon	<100

To prevent pH drops due to absorption of CO_2 from the air, the ink was buffered with Na_2CO_3 to maintain a pH of 10.0 or higher. This eliminated filter clogging due to dye insolubility.

We also observed filter clogging due to biological growth. Unprotected ink is a good medium for spore germination since it is water based and has the nutrients required for growth. Although biological contaminants are removed by filtration during manufacture, contamination by spores and bacteria occurs continuously during ink recirculation, because the stream is exposed to air. Filters in the system could not be relied upon for removal of biological contamination because growth of the bacteria or fungus would clog the filter that removed it. The ink, therefore, had to be protected by a biocide.

The initial biological problem encountered was a fungal growth observed on a filter. This was controlled by

adding a fungicide. Later, filter clogging occurred even with the fungicide present. This proved to be due to bacterial growth against which the fungicide is not effective. A screening program to control both fungi and bacteria with a biocide was instituted and several compounds were selected for further study. From this group, the most effective was selected. While heavy contamination with spores had occurred, no growth of fungi or bacteria was observed in inks protected with the biocide. With the protection provided, the ink developed showed no tendency to clog filters.

Nevertheless, corrosion of parts in the ink circulation system constituted a further source of filter clogging [5].

Nozzle deposits

After long periods of daily operation, some nozzles exhibited reduced jet diameter or deflected streams. Scanning electron microscopy revealed an amorphous, inorganic deposit in and around the orifice; x-ray analysis proved this to be a calcium salt, probably calcium carbonate. The problem was observed only sporadically at ambient temperature and humidity. To study this phenomenon, tests were conducted at 38°C and 10 percent relative humidity. This study showed that deposits formed while the stream was shut down, rather than while it was running; noticeable deposits were found to form overnight.

Examination of the ink showed calcium to be present at 6 parts per million (ppm), which is considerably less than the concentration expected. This suggested that the ink was saturated with calcium carbonate and that the excess had been removed in filtering. Examination of the literature [6] revealed that, indeed, the saturation concentration of calcium carbonate occurs at 6 ppm of calcium.

The mechanism of deposition was now clear. When water evaporated at the nozzle tip, the concentration of calcium carbonate increased beyond the saturation point and a deposit formed. The deposit could not redissolve when the stream was restarted, since the ink was already saturated with calcium carbonate.

An ink prepared with dye from which most of the calcium had been removed caused no deposits. Such dye purification is a costly process, however, so an alternative method of calcium "removal" was tried: A material was added to chelate the calcium ions, thus preventing the formation of insoluble calcium salts. This proved to be as effective as removing the calcium by purification of the dye. Whereas other heavy metal ions are present as dye contaminants, no evidence of their deposition on the nozzle has been observed.

Deposits of metal silicates were also observed on nozzles in cases where the ink was contaminated by storage in glass bottles. The silicon concentration had to be maintained below 5 ppm to prevent this. Storing and handling the ink in plastic or metal containers keeps the concentration at acceptable levels.

Functional evaluation

In addition to those requirements addressed through specific formulation variables, several other interactive properties were held within allowable limits to ensure proper system performance. These did not require additions to the formulation but rather placed constraints on the composition used and required testing of alternative materials.

• *Stream properties*

For proper drop charging and deflection, the ink stream must break into drops at a precisely controlled distance from the nozzle and must do so without the formation of very small "satellite" drops. Test methods were devised to ensure that these conditions were met at the desired operating point for all expected conditions of ink concentration, ink temperature, and stream velocity.

The term stream stability refers to the maintenance of a constant stream breakup distance. Such stability is required to preserve the required relationship between breakup time and the phase of the drop charging signal. (Long-term (minutes) drifts in the breakup distance are accommodated by the charge synchronization system [7].) Stream stability was measured in terms of the drive voltage required to maintain a stable breakup at the operating frequency and stream velocity range. This determination was made over the ranges of ink concentration and temperature expected for the system. The requirement was found to be less than 2 V, which is well below the design drive voltage.

A "print window" [8] is defined as the domain of satellite-free operation over the range of stream velocity, ink concentration, and pressure expected. Piezoelectric diaphragm drive frequency is often also included as a variable. The print window was found to be a function of ink viscosity; formulation, concentration, and temperature appear to affect it only as they affect the viscosity.

• *Ink drying*

System design requires that printed ink be "dry"—not subject to offset or smearing—within 9.5 s. This drying time must be achieved over a wide range of bond papers at various environmental conditions, including the very severe 15.56°C, 80 percent relative humidity (RH) condition.

To measure these drying times, a robot was developed that allowed the printing of a band of ink dots (the spots made on paper by ink drops); control over dot position and overlap was such that simulation of printed charac-

ters could be obtained. Print parameters were so chosen that printing this band required 30 s, allowing exploration of the range of drying times from 0.2 to 30 s with a single procedure.

Using the robot, the drying time was found to range from 1.5 to 30 s or more over the range of bond papers and environmental conditions. The mean drying time at ambient conditions (nominally 22.2°C and 50 percent RH) for a sample of 88 bond papers was found to be approximately 9 s. At 15.56°C and 80 percent RH, the mean rose to 20 s. This range was clearly in conflict with an allowed time of 9.5 s, even at ambient conditions.

Several means of accelerating ink drying were considered; these included specifying papers that would dry in the allotted time, reformulation of the ink, and forced drying by heating or other means. Since papers that dried rapidly produced poor print quality due to feathering of the ink drops and to ink spattering around the printed characters, paper selection was quickly eliminated. ("Feathering" is uneven spreading of the edges of ink dots, causing a ragged appearance in the print. "Spatter" consists of small ink dots around each character caused by the impact of drops on the paper, particularly of incoming drops on dots already on the paper.) In addition, a large variation in drying time was observed among lots of the same brand of paper.

Ink reformulation efforts met with similar difficulties. Detailed formulation studies showed that significant improvement was not achievable by changing the levels of various components. The addition of penetrants to the formulation did reduce the drying time to acceptable levels, but print quality was sharply reduced by excessive spreading of the ink drops, which produced line broadening, feathering, and spatter. In addition, the effect of the additives varied greatly among papers, having little effect on drying time on some but causing extreme growth in dot size on others. For these reasons, the formulation approach was abandoned.

The application of heat before and after printing was then considered. Heating the paper before printing (which would presumably drive out moisture from the paper) was ineffective. Paper dried in an oven for several hours also failed to show any improvement in drying. However, heating the document immediately after printing with a 350-W tubular tungsten halogen lamp, arranged to heat the paper as it was transported along the exit path, produced a substantial improvement. Whereas only three of the 45 papers in the sample dried unassisted in the required time at 15.56°C and 80 percent RH, 39 were dry after heating. At ambient conditions, all 45 dried in 9.5 s or less. Print quality was not adversely affected by this post-heating. This approach appears to be effective with virtually all papers at all required environmental conditions.

• *Evaporative losses*

In jet printing, most of the ink drops generated are sent to the gutter and returned to the reservoir for reuse. In the present system, nearly 98 percent of these ink drops are recirculated; therefore, the number of recirculations may be 40 or more. Each time the ink is exposed to air in this process, some evaporation occurs. After many recirculations, especially at high temperature and low humidity, the concentration of nonvolatile materials rises to an unacceptable level. The upper limit on concentration is set (in this case) by the viscosity that can be accommodated by the ink circulation system.

Two methods could be employed to maintain the ink concentration below the upper allowable limit: The ink could be replenished with the component that evaporates (in this case, water); or the ink supply could be replaced when the concentration reached the allowable limit. The latter, simpler scheme was selected.

A disposable ink supply container is used that is replaced after some fraction of its initial volume has been used. The volume to be used was chosen so that under worst-case conditions the concentration could not exceed the allowable limit. This, in effect, limits the number of times the ink is exposed to evaporative losses.

To set the volume to be used, the evaporation rate and the fraction of ink to be recirculated had to be known. Calculation of the evaporation rate for drops in free air at worst-case environmental conditions (37.8°C, 8 percent RH) gave alarmingly high values. However, a circulation robot equipped with the various electrodes that surround the stream gave much more acceptable rates, due, no doubt, to the shielding effect of these electrodes. The rate estimated for the printer is 400 mg/h. Given the ink flow rate and an upper acceptable limit of nonvolatile materials (yielding a viscosity of 3.0 $\mu m^2/s$ at 15.56°C), it can be shown that using only two-thirds of the initial volume of ink in the supply container prevents reaching excessive concentrations. This is the method used.

• *Print quality*

Print quality in a jet printer involves many parameters. However, if the placement of ink drops on the paper is assumed to be correct, these parameters reduce to a few characteristics of the interaction between ink and paper: optical density of print, size and shape of individual ink dots, and spatter.

All these characteristics can be measured independently of character printing and, in fact, the development of this ink was conducted largely without the use of a printer. Optical density and dot characteristics were measured on single ink dots printed on the drying-time robot using a wide variety of bond papers. This technique was used to select the drop size required from the drop gen-

Table 4 Ink properties.

Viscosity	1.79 $\mu m^2/s$ at 22.2°C
Resistivity	60 Ω-cm
Surface tension	39 dynes/cm $\left(3.9 \times 10^{-2} \frac{N}{m}\right)$
Specific gravity	1.043
pH	10.2

erator. The dot size required is 0.15 mm, the distance along diagonals between dot centers for 240 dots/in. resolution. Dot sizes were measured on a set of bond papers with various drop sizes, and the mean dot size was correlated to drop size by linear regression. The drop size required for an average dot size of 0.15 mm was then calculated from the regression equation.

Print quality was characterized by measuring the optical density and shape of individual dots on paper. Optical density varies from 1.0 to 1.1 dependent upon the paper. The shape as measured by the spot quality index varies from 75 to 87 with an average of 83. (Dot quality index is computed by dividing the smallest by the largest diameter of a dot.)

Archival properties were also evaluated; the print meets archival standards for fabric ribbons (Federal Specification DDD-R-311F), and the ink meets the standards for archival writing ink (Federal Specification TT-I-0521a).

Summary

An ink for an ink jet printer has been formulated that meets the objectives established for it (see Table 1) with the exception of drying time. Table 4 lists some of its physical properties.

Satisfactory print is produced on a wide range of bond papers, despite the marked differences in their behavior with respect to water-base ink. The ink contributes to the convenient, reliable operation of the printer in that virtually all crusting, clogging, and corrosion problems have been eliminated. These objectives have been achieved at minimum cost, using readily available materials.

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