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Materials Selection for an Ink Jet Printer

Abstract: An ink jet printer includes a system of parts that supplies, filters, pumps, circulates, and pulses a jet of ink. These parts, made of various materials (metals, plastics, rubbers, adhesives), must satisfy the mechanical and electrical requirements of the system while being compatible with the chemical composition of the ink. This paper describes the selection and evaluation of these materials for a particular ink and printer design.

Introduction

The ink in an ink jet printer comes in direct contact with the hardware that supplies, filters, pumps, circulates, and pulses the jet. Thus, many materials (metals, plastics, rubbers, adhesives) had to be selected that were compatible with this unique chemical solution. Since no interactions could be allowed that might adversely affect performance, materials compatibility was the basic materials objective. Formulation of the ink to meet its requirements was the more difficult materials problem, so materials for the printer were selected or modified based on their compatibility with the ink.

The ink developed for this printer [1] is incompatible with many materials. It is primarily aqueous and includes a water-soluble polymer to control viscosity, an aprotic organic solvent with a high dipole moment, a water-soluble black dye, a biocide, and a chelating agent. The ink also contains compounds that are known to react with organic materials, as well as inorganic ions that can interact with metals. The pH level is maintained at 10.3 with a carbonate buffer. Since there is no similar solution in common use, compatibility data do not exist.

Ink-hardware interactions can have adverse effects on both the ink and the hardware. These effects can occur either rapidly, causing immediate failures, or slowly, decreasing reliability and performance of the system.

This paper discusses the materials evaluation effort, which was divided between compatibility testing of experimental materials and materials failure analyses of problems encountered during machine development. Material design guidelines and a list of acceptable materials formulated from these studies are included.

Selecting candidate materials

In our materials compatibility program we assumed that the degree of chemical interaction permitted between ink and another material should depend on the criticality of the function of the material in the overall system. Plastics, rubbers, and adhesives may swell, embrittle, soften, or disintegrate because of chemical action induced by the ink; metals and ceramics may corrode. More important, any of these materials may contribute something detrimental to the ink, either in solution or as debris particles. This contamination can cause nozzle failure due to clogging by particles or deposits or ink failure due to changes in the physical properties of the ink.

As a first step in selecting candidate materials, we assumed that ink-hardware interaction is unacceptable if it results in contamination and/or formation in the ink of particulate or colloidal material that collects on a 5-μm filter or plugs a 25-μm nozzle orifice. It is also unacceptable if it results in dissolution into the ink of elements that consume the chelating agent, change the pH level more than 0.1, or change surface tension or viscosity.

Several experimental techniques were devised to identify the types of materials that are compatible with ink. The machine environment was simulated under controlled conditions to monitor the long-term interactions between materials and ink. These experiments consisted of chemical analyses of changes in the ink, observation of changes in physical properties of materials, and electrochemical corrosion measurements. Initial results allowed tentative selection of materials for prototype machine parts. Later these findings were compared with long-term experimental data. More specific considerations follow for particular classes of materials.

• *Metals*

Nozzles, valves, pumps, filters, fittings, and other structural parts in the plumbing system of the printer are fabricated from metals; corrosion is a potential problem

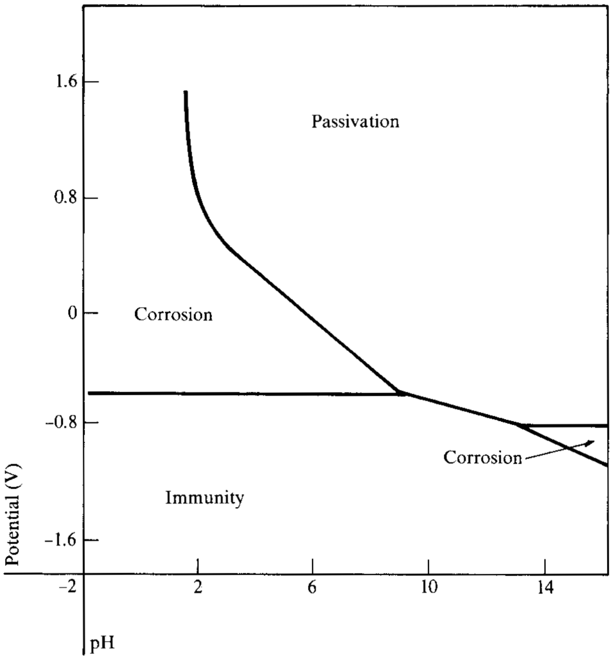

Figure 1 Pourbaix diagram for iron.

when these parts are exposed to ink. Failures may occur due to mechanical weakening, leaking of ink pressure, and/or blocking of the ink flow by debris. Thus, alloys were selected for their resistance to uniform corrosive attack, pitting, and crevice corrosion.

Some metals resist uniform corrosive attack from aqueous solutions by forming a surface oxide film that chemically arrests further attack. This passivation occurs spontaneously under certain environmental conditions and is a principal factor in the corrosion resistance of stainless steel alloys. We predicted that the basic pH level of the ink would enhance passivation in standard austenitic stainless steels. Metals protected by passivation, however, are usually susceptible to localized film failure (pitting) when subjected to chloride ions. And pitting is a greater hazard than uniform corrosion attack because the concentrated action can quickly produce a catastrophic failure. Since the ink contains sodium chloride from the ink dye, stainless steels were evaluated for their resistance to pitting.

The standard austenitic stainless steels (18% chrome, 8% nickel) were initially selected for the prototype metal parts that contact the ink solution. This selection is supported by a Pourbaix diagram (Fig. 1), which reveals that spontaneous passivation of iron should occur in the basic pH level of the ink.

- *Polymers*

Polymeric materials were selected for resistance to attack by the ink. Immersion in the ink can cause swelling, softening, embrittlement, or stress cracking of polymeric components, which in turn might cause functional failures. Stress cracking can occur in either of two ways. Ink of original composition (dilute), as it contacts an immersed component, can cause stress cracking. When ink is allowed to dry on the surface of a component, preferential evaporation occurs and the organic constituents of the ink can become more concentrated. These constituents can then cause stress cracking of certain polymers, even though they would not have done so in the dilute solution.

All polymeric materials that are not highly subject to hydrolysis were considered candidates for long-term compatibility with the ink, since interaction with the dilute nonaqueous components of the ink could not be predicted. The initial machine design was reviewed, and the most likely polymers (thermoplastics, thermosets, rubbers, foams, adhesives, and sealants) that could be used for fabrication of parts were selected for compatibility testing. Alternative polymers and some polymers that were considered generally interesting were also evaluated.

- *Ceramics*

Ceramic materials must resist corrosion or dissolution, which can be induced in most glass or silicon-based ceramics by the basic pH level of the ink.

Ceramic materials were considered for nozzle and driver piezoelectric diaphragms. The choice of a nozzle material depended on three factors: the manufacturability of dimensionally reproducible nozzle orifices; the wear resistance of the material to the jet; and its resistance to corrosion or dissolution by the ink. The basic pH level of the ink is detrimental to most glass or silicon-based ceramics. Specific glass materials—zirconium silicate, boron silicate, alumina, and a machinable glass ceramic—were thus chosen. Flint glass was used as a reference material. A lead zirconium titanate ceramic was evaluated for the piezoelectric driver diaphragm.

- *Electrical circuit materials*

Electrical components must be protected from the ink to avoid chemical reactions that can produce short circuits, grounding, or resistance failures. Each component was evaluated separately for stability in its particular environment (ink immersion, ink spatter or mist, or atmospheric conditions).

Design of experiments

- *Metals testing*

Procedures were selected to experimentally evaluate the susceptibility of metals to corrosion in the ink solution, especially the pitting and crevice forms of corrosion.

Test procedures consisted of direct observation of physical properties and electrochemical experiments. When combined with the more rapid electrochemical testing, direct observation experimentation, though slow and subjective, offered greater comprehension of system corrosion.

Metal samples were selected to represent a range of corrosive conditions, including galvanic couples of different metals, crevice bindings of similar metals, metallic platings and surface treatments, and others. These were periodically withdrawn from the ink solution and monitored for corrosive attack. After extended submersion of the metals, weight loss measurements indicated uniform corrosive attack; microscopic examination revealed localized attack.

Because the corrosion of metals requires the transfer of electric charge, corrosion behavior can be predicted by electrochemical experiments such as galvanic and potentiostatic measurements. A relative galvanic series of metals in the ink was determined by comparing the electrical potential formed between a standard chemical cell and various metallic electrodes. Normally, selection of metals on the lower, more active end of this series would be avoided. The polarization trace of current from a sample as a function of imposed potential predicts the corrosion rate for metallic parts in solution. The results from the corrosion experimentation provided a range of behavior for metals in the ink. These data, along with the failure analyses and experience with prototype machine hardware, formed the basis for the final selection of metals.

• *Evaluating polymers*

Most thermoplastic samples were molded into tensile specimens. Most rubber samples were purchased O-rings, but some were tensile specimens die-cut from purchased slabs. Epoxies were cast into blocks or tensile specimens. All foams, tubing, thermosets, and some thermoplastics, rubbers, adhesives, and sealants were obtained in whatever form was available.

Polymeric samples in various geometric shapes were exposed to the ink at 24°C and evaluated in two ways:

1. Each polymeric sample was placed in an individual container with 50 ml of ink that contained all constituents except dye. The pH level was buffered to 10. The containers were constantly agitated, and the samples and ink solutions were periodically evaluated over a 30-week span. Evaluation consisted of differential ultraviolet (UV) absorption measurements of all ink solutions and atomic absorption silicon analysis of those ink solutions containing a silicon polymer sample. Weight change was determined for some samples, hardness was measured on other samples, and all samples and ink solutions were observed generally.

   The differential UV absorption measurements were made to determine if any polymeric materials had dissolved into the dyeless ink. Absorption is defined as the product of path length through solution, molar concentration of the dissolved material, and extinction coefficient of the dissolved material. The change in absorption of the ink as a function of exposure time with the samples was measured over the range of 250 to 310 nm. The rationale for this experiment was that many of the base polymers or additives to the polymers contained chromophores that absorb above 250 nm. Normally, these chromophores have extinction coefficients of 100 to 10000. Therefore, an observed change in absorbance of 0.1 (10 mm path length) would be equivalent to 0.02 mg of material for a chromophore having a molecular weight of 100 and an extinction coefficient of 10000.
2. Tensile specimens, or O-rings, of some polymeric materials were subjected to a bending or tensile stress and immersed in a common bath of ink that included dye. The solution was constantly agitated and aerated. Samples were withdrawn periodically over a period of 30 weeks for tensile strength and hardness measurements and for visual inspection.

Evaluation was based on the results of both tests. Samples were considered acceptable when they did not show significant continuing changes in sample or ink properties as measured for 26 to 30 weeks (sample discoloration was not considered a failure). Changes in UV absorption of 1.0 or less that were not steadily increasing were considered acceptable. This was based on the fact that the polymeric materials that produced these data had not caused failures during long-term machine and robot testing.

Because a large number of glass-filled polyester parts were to be used, a test was performed to determine whether these materials would contribute a significant amount of silicon or calcium to the ink, which could then form nozzle deposits. Molded samples of the materials with machined surfaces were subjected to ink in polyethylene bottles. No additional silicon or calcium was found in the solutions after 13 weeks.

Many rubber O-rings are used as seals in ink jet printers. Long-term compression set in these O-rings under actual machine conditions, including exposure to the ink, was evaluated. Duplicates were obtained of each O-ring used in the machines tested. Fixtures were built to compress the duplicate O-rings to the same extent as would occur with machine use (the force required for compression was measured with an Instron Tensile Testing

Machine). The fixtures containing the O-rings were clamped shut and immersed in ink at 38°C. The compression force was measured initially and after 2, 9, 35, and 100 days' immersion. In all cases, stress relaxation stopped after either 9 or 35 days. We concluded that seals that did not leak in machines after 100 days would not leak after longer periods of time, provided an otherwise acceptable seal material was used.

Rubber stoppers are used in ink supply containers, with ink being withdrawn through a needle inserted through the stopper. The supply containers are removed from the machine before they are empty and replaced. In addition to being compatible with the ink, the stopper material must instantly seal upon withdrawal of the needle. Several candidate materials were molded into stoppers and inserted into containers filled with ink. Needles were inserted and withdrawn after the 15th, 30th, and 60th day, and the stoppers were inspected for leaks. A silicone rubber material proved acceptable.

- *Ceramics testing*

Six ceramic materials and four ceramic-to-metal adhesives were tested in ink at three temperatures: 21°C, 43°C, and 60°C. The corrosion rate was measured by sample weight loss and ink analysis for the dissolved elements (silicon and others). After 2000-3000 hours, the samples were examined by scanning electron microscopy/energy dispersive x-ray analysis in an attempt to understand the process of corrosion attack. All tested silicon-based ceramics had some corrosion rate; however (as shown in the Results), one was acceptable as a nozzle orifice material.

- *Electrical circuit compatibility*

Compatibility experiments for electrical components, such as the charge sensor and the container contact [2], were devised. The charge sensor required insulation for its electrodes. Candidate insulation coatings, both organic and ceramic, were evaluated on sample circuits immersed in ink for 30 days. Coatings were considered unsatisfactory if ink could penetrate them and modify the performance of the sample circuits. Chemical degradation, moisture absorption, coating pinholes, and poor sealing were common problems resulting from unsatisfactory coatings.

An ink container electrical contact testing program was devised to ensure that environmental corrosion of the contact would not occur. Because the ink container is disposable, expensive contact metals are undesirable; however, inexpensive copper-base metal contacts tarnish in the machine environment. Potential contact materials and coatings were subjected to concentrated environmental gases to accelerate evaluation of tarnish and oxidation resistance as determined by contact resistance measurements. Two gas combinations were used for a 2000-hour exposure: vapors of flowers of sulfur and water formed in a closed chamber at 63°C; and a dilute combination of flowing hydrogen sulfide, sulfur dioxide, and chlorine gases. For this contact design, the stability of contact resistance is more important than the magnitude of contact resistance; samples from this experiment were evaluated on this basis.

Development experience

The materials experience gained from prototype machines was invaluable in successfully selecting materials for production printers. Most problems resulted from complex combinations of materials and operating conditions that were difficult to simulate or anticipate. These problems were solved by analyzing development machine failures.

- *Corrosion*

The diaphragm housing (the primary structural metal part in the jet printer head) provides a seat for the piezoelectric ceramic diaphragm that vibrates the ink jet. This housing was the victim of two major corrosion problems, which were so severe that they disabled every printer because of continued nozzle clogging.

The housing was first fabricated from free machining grade stainless steel (this alloy contains manganese sulfide inclusions that make the alloy easier to machine). When a group of housings were chemically polished to smooth the surface of the housing ring and provide a better seat, the chemicals attacked the manganese sulfide inclusions and left small pits in the housings. After these housings were installed in the machines, crevice corrosion, initiated in the pits, quickly grew until widespread corrosion in these areas produced enough debris to clog the nozzle. All crevice corrosion occurred at the inclusions parallel to the rolling direction of the metal, instead of perpendicular to the metal surface as in common pitting. Although corrosion was often related to pitted parts, not all failures could be directly traced to diaphragm housings that had been chemically polished; therefore, the free-machining stainless alloy was replaced with the basic austenitic stainless alloy in all parts that contact the ink.

Later, the diaphragm housing again became the target of corrosive attack because of a change in electrical operating parameters. The housing is grounded and, through the ink, provides one electrode to the piezoelectric diaphragm. The operating point caused the crystal housing to be charged positively relative to the ink, and the metal dissolved as general corrosion on the housing ring. With the high capacitance of the piezoelectric diaphragm, the net charge flowing through the crystal housing was greater than current density levels used in electroplating. This problem was resolved by changing the drive voltage to an alternating signal with no net flow of charge.

A similar corrosion problem became apparent in the valve; the attack was caused by an electrical potential from outside of the plumbing system. Two parallel stainless steel valve reeds were operated by an actuator block on the end of a solenoid-driven pin. Either through induction or by short-circuiting of the pin to the solenoid lead, an electrical circuit was established through the valve and each component was polarized into local anodes and cathodes. Corrosion was observed on each of these components, either at the local anode or on the positively charged section. Failure resulted when debris blocked operation of the valve. Insulating the hardware in the valve system resolved this problem.

Pump failure was a major concern because of the possibility of corrosion of the miniature nickel pressure bellows, which is fabricated by electroforming. Because it is only a few micrometers thick, the bellows is quite susceptible to catastrophic corrosion, either through penetration pitting or through mechanical weakening, leading to fatigue cracking. The first failures were experienced after the bellows was short-circuited to an electrical lead and the resulting potential produced a few large pits that penetrated sufficiently to cause a leak. This problem was resolved by electrically isolating the bellows. Other failures occurred when a few bellows were quickly attacked by the ink during testing. The problem was traced to recrystallization from overheating during a soldering operation. Because nickel parts dissolve slowly into the ink, we concluded that longer-term mechanical failures could be expected. Because electroforming is almost exclusively limited to nickel, the only means to protect the bellows from corrosion was to cover it with a noble metal plating such as gold or paladium, or with a polymeric coating.

- *Gutter*

The plastic gutter catches the continuous stream of ink drops that are not allowed to reach the paper and funnels them back to the ink supply. In developmental printers, several requirements were established for this part, i.e., ink compatibility, transparency, and a thin blade to catch the drops. The blade material had to have good moldability for manufacturing reasons, toughness, and creep resistance, because it is subject to handling for cleaning and adjusting. Initially, several materials were used to make the gutter, including nylon 11 and polycarbonate, which met all the requirements. The materials were compatible with the ink only when immersed, however, and not when sprayed and allowed to dry. Preferential evaporation caused concentration of organic ink constituents and subsequent stress cracking of the gutter. Eventually, the transparency requirement was dropped, and several plastic materials met all requirements. However, as a result of the series of failure analyses, the importance of preferential evaporation was discovered, and the need was established for its evaluation on parts that were subjected to ink contact other than immersion.

- *Nozzle deposits*

During machine shutdown, the ink in the nozzle orifice is subject to evaporative losses. Trace components of the ink that are at some equilibrium solubility (i.e., calcium carbonate and aluminum silicate) precipitate at the exit of the nozzle orifice when the equilibrium solubility is exceeded after evaporative losses. Deposits of calcium carbonate and aluminum silicate were observed in nozzle orifices after shutdown periods. The amount of deposit depended on the concentration of precipitating ions in the ink, and on temperature, humidity, and the number and length of shutdowns. The nozzle deposit problem was corrected by adding a chelating agent to prevent the formation of calcium deposits and to maintain the concentration of silicate ions and aluminum at satisfactory levels. This problem emphasized the need for preventing the transfer of trace levels of contaminants from machine materials to the ink. This is especially true for materials with limited solubility in ink and for ions that would consume the excess chelating agent.

Results

Through compatibility experimentation and analysis of failures that occurred in prototype machine testing, acceptable materials were identified and their performance rationalized, generating a set of design guidelines for the use of these materials in the printer.

- *Acceptable materials and rationale*

The basic metal selected for continuous exposure to jet printer ink is austenitic stainless steel. This alloy offers satisfactory protection from all forms of corrosion attack, although some design precautions were necessary to control galvanic and crevice attack. Pitting, initiated by the salt content of the ink, was not a problem because of the beneficial pH level.

Metal parts that are not continuously exposed to ink can be protected from corrosion by electroplatings and coatings that rely on oxidation protection. Black oxide and chrome plating were selected for the protection of carbon steels, and aluminum is protected by anodization. Other traditional electroplatings, such as nickel and zinc, are unacceptable. This is consistent with the passivation behavior of metals at higher pH levels.

Polymers that proved acceptable during compatibility testing and in machine use are listed in Table 1. In gen-

Table 1 Acceptable Polymeric materials for ink jet printer.

Thermoplastic molding compounds	polypropylene polyethylene rigid PVC Polyester acetal acetal-TFE filled polystyrene-polyphenylene oxide blend
Thermoset molding compounds	phenolic epoxy
Rubbers	some fluoroelastomers some silicones some ethylene propylenes
Tubing	polyethylene vinyl acetates
Adhesives & sealants	some epoxies some silicones

eral, those polymers (polyethylene, polypropylene, and others) that are resistant to the organic constituents of the ink in concentrated form are compatible with the dilute ink solution. Incompatibility would have been predicted for most polymers with the concentrated organic constituents, but predictions could not be made when these constituents, in dilute form, were placed in contact with the polymeric samples. For this reason, all polymers that are not highly subject to hydrolysis were considered candidates. Cellulose acetate was the only polymer tested that is highly subject to hydrolysis. It failed, as expected, with the largest change in UV absorbance of any sample tested.

A commercially available zirconium oxide containing alkali-resistant glass was the only acceptable ceramic nozzle orifice material for both manufacturability and corrosion resistance. The zirconium-silicate glass had a measurable corrosion rate at elevated temperatures (60°C); however, the rate of corrosion decreased with time. The nonlinear corrosion rate is influenced by a decrease in ink pH due to hydrolysis of one of the ink components at elevated temperatures. SEM/energy dispersive x-ray examination of the zirconium-silicate glass does not show measurable topographical changes nor significant composition changes.

Four materials were evaluated as adhesives for ceramic-to-metal or ceramic-to-ceramic bonding. The materials included three lead or zinc-based silicon glasses and a cobalt-nickel-iron alloy. All of these materials proved to be unacceptable because of excessive corrosion in ink, especially at higher machine operating temperatures.

• *Design guidelines*

The following design precautions were used with metallic parts to ensure protection from corrosion: We used the same alloy throughout, avoided stagnant areas in the ink plumbing flow, and controlled stray electrical currents.

Using the same alloy prevents galvanic corrosion created by the solution potential difference between two dissimilar metals; that is why several stainless steel alloys could have been used but not in combination. When a different metal or alloy must be used, it must be electrically insulated from all other metal parts. Stagnant areas in the plumbing system can lead to crevice corrosion induced by concentration cell effects. Normally, this is not a concern unless the ink can seep into or behind a gasket or a loose-fitting joint. As may be seen from the numerous examples, stray electrical current may charge metal parts positively relative to the ink solution, thus permitting corrosion.

Selection of polymeric materials for design of the jet printer was made by using the acceptable materials listed in Table 1. Generally, polymers were selected for specific applications. Polyester or a polystyrene-polyphenylene oxide blend, with or without glass filling, was used for creep-resistant, high-strength structural components, or where flame retardance was needed; rigid PVC was used for transparency or flame retardance; and acetal or fluorocarbon-filled acetal for wear resistance. Polyethylene or polypropylene was used for flexibility or the capability of being processed by blow molding. Polyethylene-vinyl acetate was used for tubing applications. Ethylene-propylene rubbers (types that proved compatible) were used for rubber seals because of their low cost and good resistance to compression set.

Selection of ceramic materials for critical applications was based on some unique property of the material with respect to manufacturing or functional requirements of the component. Normally, the chemistry of the ceramic material (i.e., glass) can be adjusted to meet the compatibility requirements. Another alternative used to promote compatibility of ceramics was protective coating (i.e., plating the component with a compatible metal).

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