

Metallic Pigments: Overview and Opportunities for Digital Printing

Sarojini Deevi
Philip Morris USA, Richmond, Virginia, USA

Abstract

Advances in the short run, on-demand digital printing have brought about tremendous improvements in the quality of printing as well as the color gamut available. The use of metallic pigments in conventional printing inks to achieve exceptional brilliance and metallic effects is well known. The pigments generally used are aluminum and brass powders, which are formulated into inks. Some of the characteristics of these metal powders are summarized, and the issues associated with their use and handling as well as the particle characteristics that bring about the desired effects are reviewed. In spite of the remarkable achievements in the field of digital printing, there have not been any developments toward the use of a metallic ink. One of the reasons for this is the incompatibility of the technology used in the digital printing process, and the metallic flake pigments used in conventional metallic inks. The present paper highlights some of challenges that would need to be addressed for developing the capability to print using a metallic ink.

Appeal of Metallic Inks

Gold and silver have, since prehistoric times, been associated with an image of wealth and opulence. The art of decorating fine book-bindings, and articles made of leather with precious metal, is centuries old. Pure silver or gold was hammered into a thin foil, which was then transferred to the substrate by hand. A similar appearance is achieved in the present day world, using a far less expensive and less laborious technique, by means of high speed printing equipment, using gold and silver colored pigments that are suspended in a suitable vehicle.[1] Brass powder is used to obtain the gold effect, while aluminum is used for obtaining a silver effect. These **metallic inks** have been used to print on a variety of substrates, including packaging, to suggest added value, and impart an upscale appearance to the packaged product. Metallic inks are now routinely used to convey a broad range of images, including opulence, prestige, elegance, antiquity, exclusivity, and so on. A silver color is used to suggest a high-tech image, while gold gives the impression of luxury and richness, and that of a premium brand product; several metallic shades are available to give an enhanced image to the product.

Metallic effects have been achieved by several ways in printing; for example, metallic powders can be used for "bronzing", whereby the dry powder is applied to a wet size coating. The most common method of achieving the metallic look is the use of a printing ink containing metallic pigments. Metallic inks are currently available for the traditional print markets: flexography, gravure, offset, screen printing, web heatset, letterpress, UV, EB, and thermography.[2]

Metallic Pigments

The color and hue of any ink is due to the presence of a pigment/colorant in solution or in suspension. Dyes are soluble colorants- organic or inorganic compounds which dissolve in the vehicle and give a brilliant color to the solution. Pigments, on the other hand, are insoluble, the pigment based inks consisting of very small particle sizes of the pigments suspended in the vehicle, as a dispersion. The pigments in black ink are carbon black, while metal powders or flakes are the pigments in metallic inks). To ensure that the particles do not coalesce and separate out of the dispersion, dispersants are added, which, by various means (chemical or steric), keep the particles from approaching each other.

The metallic pigments in common use are aluminum powder, bronze powders, and copper powder. Aluminum powders are used to give a silver effect, while bronze powders are used for achieving the brilliant appearance of gold. Bronze powders are alloys of copper and zinc, and the zinc content of the alloy is varied to change the shade of the gold (they are essentially brass powders, since bronze is an alloy of copper and tin),

Rich gold	70% Cu - 30% Zn
Rich pale gold	80% Cu - 20% Zn
Pale gold	90% Cu - 10% Zn
Copper	100% Cu
Silver	Aluminum powder

The different shades of metallic inks have been incorporated into the Pantone Color Matching System, which assigns PMS numbers for six shades of gold, PMS 871 to 876, the shades corresponding to the higher numbers showing greater intensity of the copper color; and PMS 877 is silver.

Metallic pigments are generally manufactured by atomization of the molten metal/alloy, which results in spherical shaped powders. These are then ball milled to

obtain flakes. Some pigments for extraordinary brilliance call for very thin films, which are made by evaporation of the metal on to a substrate, and the substrate is later dissolved. The particles are flat platelets, and give the effect of micro mirrors, and enhanced reflection.

Metallic Inks Used for the Traditional Print Markets

Some of the major manufacturers of metallic pigments/inks are Eckart, Wolstenholme, Pantone, Ecosse, Van Son Holland, Keane Graphic Products, Avery Decorative Films, United States Bronze Powders, Ault and Wilburg Inks,and Coates Brothers.

The following is a typical analysis of silver and gold gravure inks. They are flammable liquids, and the high VOC (Volatile Organic Compounds) levels in the inks can be noted:

Silver Ink	**Gold Ink**
• Isopropyl acetate- 53%	• Isopropyl acetate-17%
• Nitrocellulose resin 17%	
• Isopropyl alcohol 11%	• Ethanol 16%
• VOC's (wt.%) 64	• VOC's (wt.%) 35
• Density (1.05 g/cm3)	• Density (1.28 g/cm3)

There has been tremendous pressure on the ink manufacturers to reduce the level of volatile organic compounds, and develop more environmentally friendly inks.[3] This led to the development of water based and UV curing formulations.[4] Earlier water based inks were two pack systems, which were mixed just prior to printing. Problems with inconsistency (due to inaccurate mixing), limited the life of these inks to shorter print runs. Also, they had limited stability, once they were mixed, and had to be used in a relatively short time. Product improvements have resulted in the development of one-pack, ready to use inks. At present, single pack systems are available, which can be used ready from the can. The single pack systems have properties comparable to solvent formulations, with health and safety advantages.[4]

Water based gold ink formulations for gravure printing have a copper content ranging between 21 to 26%, and zinc content ranging from 3 to 9%, depending on the particular shade of gold.

Percent VOC's :	< 4
Percent total solids	40-45
Boiling point	212 F
Pigment content (gold ink):	28-30 %;
VOC's	4%

For silver ink, the pigment content ranges between 20-24%, and the VOC's are <2%. Metallic inks require smooth coated stocks for the best appearance. Water based inks are used in converting cheaper uncoated and coated paper and board; whereas solvent based formulations are used for the top-end gravure printing market e. g., cigarette cartons, for brilliance and line definition. Metallic inks require over varnishing for rub resistance.

Issues Unique to Metallic Pigments/Inks

Metallic inks for the traditional printing market show some major differences compared to other inks[1].

Appearance

The attractive appearance of the metallic print results from a process called "leafing". When flakes of metallic pigment are used, (the thickness of the particles is very small compared to the other dimensions), strong metallic appearance is achieved. With the proper choice of surface tension and viscosity of the ink vehicle, the particles are laid down during printing in such a manner that they overlap, and bond together on the paper. This creates a smooth shiny metallic surface. This characteristic is called "leafing"; the better the leafing, the higher the metallic luster, and the closer to a true metallic appearance. Smooth coated substrates are a requirement for a good quality print, since superior leafing can be achieved on these. On rough stocks, more impressions might be needed to offset absorption of the ink. Non-leafing metallic grades are also available, and these are used for obtaining different degrees of sparkle and brightness.

Particle Sizes

Coarse metallic particles will give brighter appearance. Finer particles tend to give a lower brightness, but very good definition of print and opacity can be obtained with finer particles.

Particle Shapes

Flat, thin flakes for leafing and good luster**.**

Particle Size Distribution

Narrow particle size distribution results in brighter shades.

Ink Mileage

Lower than that of conventional inks. Silver ink is easier to run than gold-bronze, hence it is in more common use.

Reactivity/Pyrophoricity

Metallic pigments should be handled carefully, since metal powders are very reactive, and can easily ignite, causing fire/explosion hazard. They also tend to get air-borne very easily, and metal dust is an explosion hazard.

Corrosion/Tarnishing/Gassing

Metallic pigments react with water, with the evolution of hydrogen. This problem of "gassing" can lead to build-up of pressure in the can. They are susceptible to corrosion, leading to tarnishing of the surface and loss of brilliance. Though resins are added to slow the corrosion, it is still a problem. To prevent tarnishing, the powder may be coated

with fatty acid, or corrosion inhibitors can be added. In the case of aluminum, special passivated pigment has been developed to avoid gassing or hydrogen evolution.[3]

Ink Jet Printing

Digital printing addresses the on-demand, variable content, short-run printing market, which has seen significant growth in recent years. Of the several technologies that have been utilized in developing printers for this printing segment, ink jet printing has evolved into a valuable process for the industrial marking applications as well as the home and office printers. Wide format printing of graphics for the display market has also developed into a specialty segment. The technique is a non-impact process, and essentially consists of jetting a stream of ink droplets on to a moving substrate.[5,6] Its main advantages are the capability for high speed printing of variable data. Advances in this printing technique have led to superior print quality at low cost. While print quality is very good in the wide format printing, the speed of printing is not close to that obtained in industrial printing. Also, while the ability to print metallics is available with the traditional processes, it is not available with the digital printing techniques. As the quality of printing continues to improve, customers will come to expect printing quality that matches traditional printing processes, like gravure or offset printing. One of the ways of adding value to the short run/variable content digital printing will be the capability of printing with metallic inks.

The main inkjet printing techniques available to date are the continuous inkjet, and drop on demand. In the latter category, the ink drops may be produced by the bubble jet technique where the inks are subjected to rapid increase in temperature by the use of a heater that generates a bubble and ejects the ink. Alternatively, the ink drop is ejected by changing the volume of the ink in the chamber by a piezoelectric device. The inks used for printing by the ink jet technique have special requirements, based on the mode of droplet generation.

Ink Requirements for Ink Jet Inks

Viscosity of about 4 cP is required for continuous inkjet inks versus upto 20 cP for drop on demand mode. Conductive inks are required for continuous inkjet inks. They are usually water based, since they can be made electrically conducting by the addition of salt; oil or nonaqueous based inks are not suitable since it is difficult to dissolve high concentrations of salt in these. Conductivity is not required for inks in the heads utilizing drop on demand mode.

Oil/nonaqueous base inks contain nonvolatile vehicles e.g. glycols, fatty acids/esters, and they have the following advantages: no problems with first drop delay/long term maintenance, low toxicity, minimal corrosive effects, and low volatility. Since the viscosity is higher than that of waterbased inks, they are useful for piezo printheads. Additionally, the inks used in bubble jet printheads should withstand rapid temperature rise cycles without deterioration.

All the inks usually contain humectants to reduce evaporation. Drying of water based inks is by a combination of evaporation and absorption. Drying of nonaqueous inks is by absorption into the paper fibers; since ink bleeding is a problem, they require clay-coated ink jet paper

Challenges in Developing Metallic Inks for the Ink Jet Printing Market

As compared to the inks for conventional printing processes, the ink jet printing process demands special considerations as to the nature of the pigment, as well as the ink as a whole. One of the advantages of traditional printing is the exceptional color gamut, superior graphics, and metallic effects that can be achieved. The cost for this is reasonable, since the ink is relatively inexpensive, and the equipment is rugged. The cost per print decreases dramatically as the run size increases. The cost of printing digitally using sophisticated equipment/nozzles is higher, as is immediately apparent.

The technology for printing metallics in the inkjet printing market is unavailable. Development of metallic inks for the ink jet printing process requires addressing a whole new range of issues. Most of the inks used for digital printing are based on dyes, which are soluble. Pigmented inks are available for digital printing, and these have the advantage of precise color, color fastness and water fastness. Submicron size pigments are used in these inks, and their size ranges in the tens to hundreds of nanometers. For obtaining good resolution in the printed image, small ink droplets should be used, which is generated using small orifice nozzles.

When metallic inks are used in conventional printing, the brilliance of the printed image is achieved by using large metal particles. When the metallic pigments are reduced in size, their brilliance is diminished. These opposing characteristics of the size of the pigment required for brilliance of the printed image, versus the limitation of the small droplet size required for good resolution should be resolved for printing with metallic inks.

The inks used in traditional printing are very inexpensive compared to ink jet inks, since the latter have to be formulated to tight requirements of purity, so as to avoid any damage to the printhead. Filters have to be incorporated at several points to trap large particles which can clog the nozzle. Digital printing is therefore a more expensive process, and the printers do not expect any enhancement of value in substituting an established technology for a sophisticated, more expensive technique. This is one of the main reasons why technology developers have not addressed the use of metallic ink in digital printers.

Steps Involved in Formulation of a Metallic Ink Jet Ink

The steps can be grouped under three broad categories:

1. Relation of pigment characteristics to the appearance of the print

2. Studies on droplet behavior
3. Choice of printhead and ink formulation

Relation of Pigment Characteristics to the Appearance of the Print

Since a choice of particle size of pigment has to be made for brightness versus ease of jetting, it would be necessary to identify the range of particle size of the pigment that would give satisfactory appearance on printing. The nozzle diameter should be large enough that particles do not clog it easily. *Nozzle clogging has been reported to be a problem even for the pigmented inks containing particles in the tens and hundreds of nanometers size range.* This would be a more serious problem with metallic pigments.

The shape of the powders is crucial to the effect obtained in printing. The effect of different shapes and aspect ratios of the pigment on the appearance of the print should be evaluated. Particle size distribution of the metallic pigments should be unimodal- i. e., a narrow size range with no large particles. Additionally, filters have to be incorporated in the system to capture any occasional large particles, before they reach the nozzle. Alternately, modes of printing without the use of nozzles may need to be explored.

Studies on Droplet Behavior-Influence of Nozzle Characteristics

The feasibility of obtaining stable and uniform droplets of the ink will need to be evaluated. The effect of nozzle geometry, orifice size, and other characteristics of the nozzle on the behavior of the jet should also be addressed. In addition, it is not known how the presence of a metal particle in the droplet affects the charging of the drops, and how that would impact printing in the continuous ink jet mode.

Choice of Printhead and Ink Formulation Ink Formulation

Once the feasibility of utilizing one of the inkjet technologies to print with metallic inks has been demonstrated, a suitable print head/nozzle should be identified. Since metal particles are abrasive, the printhead material chosen should be resistant to wear leading to changes in the shape and size of the orifice.

Ink formulation, which is the next step, would comprise the following: identification of the effective methods of stabilization of the dispersions, including the polymers that may be used, that will be effective at the particle sizes of the metallic pigment chosen, for making ink formulations. In addition, choices of solvent/vehicle composition, viscosity adjusters, etc., need to be made.

In summary, the effect of particle sizes, shapes, orifice size, and nozzle geometry on the appearance of the print should be correlated, and the pigments which will give satisfactory appearance, with minimal nozzle problems should be identified. A stable formulation should be run through a nozzle, and studies on jetting, droplet formation, jet breakup behavior, and stability of the stream should be carried out**.**

Summary

The state of the art of metallic inks used in the traditional printing processes has been summarized, and some of the issues associated with metallic inks have been highlighted. Currently there are no printers on the market, which can print using metallic inks, and none of the digital printer companies presently offers digital /inkjet printing of metallic inks.

References

1. Frank F. Yeager, *Printing Impressions*, **22**, No.5, pp15, 71 (1979).
2. Alan Carey, *Paper Board Packaging*, **73**, No.10, 68-70 (1988).
3. Paul Fallon, *European Journal of Polymers, Paint, Color* **183**, No. 4339, pp526, 528-529, 532 (1993).
4. Michael Yates, *Pigment & Resin Technology*, **24**, No.5, 3-5 (1995).
5. Hue P. Le, *J. Imaging Sci. and Technol* **42**, No.1, 49 (1998)
6. Walter Crooks, and Francis C. Lee, in Ullmann's Encyclopedia of Industrial Chemistry, Volume A13, Fifth Edition, 1989, VCH Publishers, New York, pg. 588.

Biography

Sarojini Deevi received her Ph. D. in materials science from the Indian Institute of Science, Bangalore, India, in 1984. Her interests have been in the combustion synthesis of industrially important materials and their characterization. Prior to that, her work involved thermal and mechanistic studies of elastomeric composites containing particulate materials. Presently her interests include digital printing techniques and metallic materials for digital printing.