

# Novel Electrophotographic Toners for Providing Metallic Effects

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## Abstract

*In order to produce toners that are capable of providing metallic sparkle and effect, a number of obstacles have to be first overcome. Since having static charge is an important requirement for toners, it is not practical to use conductive metal flakes in metallic toner formulations. This difficulty was overcome by using mica or similarly based interference pigments. These non-conductive pigments not only provide a large flat reflective surface but can be coated with inorganic and organic coatings. By controlling the thickness of the high refractive index inorganic coating over the mica flakes, the color of the reflected light changed and can be utilized to enhance the metallic sparkle.*

*These toners can be produced by minimizing the shear conditions in the extruder during the compounding of the toner components. These can be created by optimizing the compounding temperature, screw configurations, molecular weight of the toner resin etc. By imposing a convergence on the toner melt at the die exit and by controlling the draw ratio of the melt slab after the die exit, the pigment flakes can be forced to align in the process direction. The resulting toners have a flat shape as a consequence of the internal structure formed during the melt processing step.*

*Due to the large size of the pigment flakes in the finished toner, and its shape, these toners are capable of providing remarkable sparkle and metallic effects. These toners produce the metallic effect by themselves but alternatively they can be placed over or under other color toners to generate many interesting effects that were not possible before. A method of measuring the sparkle in metallic images is also described. By measuring color properties at various angles, "Flop Index" can be calculated and used to quantify the extent of metallic effect.*

## Introduction

Over the years, many attempts have been made to print metallic effects using dry electrophotographic toners. But despite many attempts to produce metallic toners in the past, most of these efforts have not been successful. Several disclosures have been made describing different methods of producing metallic toners in which the metal flakes have been first treated and used as pigment flakes [1]. In another disclosure, the treated metal oxides particles are attached to the outside surface of the toner in a separate processing step [2]. Most of these attempts have only provided insufficient metallic effects. So there is still an existing and unfulfilled need to produce toners that are capable of producing metallic appearance or sparkle.

In order to produce a toner that is capable of producing metallic effects, there are several hurdles that need to be overcome. These include:

- Electrical conductivity of pigment
- Size of pigment
- Reflecting surfaces/planes in pigment flake

- Orientation of pigments
- Manufacturing process to produce such toners

In order for a toner to function properly in an electrophotographic process, it has to be able to sustain an electrical charge for development and transfer etc. Metallic flakes can perform well in inks but when these flat flakes are used as pigments in toner, the electrical conductivity of such pigments becomes an issue. To overcome this difficulty the metal flakes are often coated with a non-conducting inorganic coating or an organic polymer resin. These attempts to coat the metal flakes, however, is only able to provide marginal benefits. Most of the metal pigment flakes are not mechanically strong and readily break-up during the manufacturing process. As pigment fractures, it exposes the conductive core which immediately affects the toner charge. Also, some coatings, especially polymeric types, can separate from the surface as a result of the elevated temperatures necessary in the melt compounding processes used in toner manufacturing. Any exposed surface of a conductive metal flake can not only reduce the charge of the toner, they can often cause charge injection when exposed to high electrical fields. A metallic toner that exhibits adequate charge/mass, may become conductive when present in the high electric fields that are encountered during a converging nip transfer.



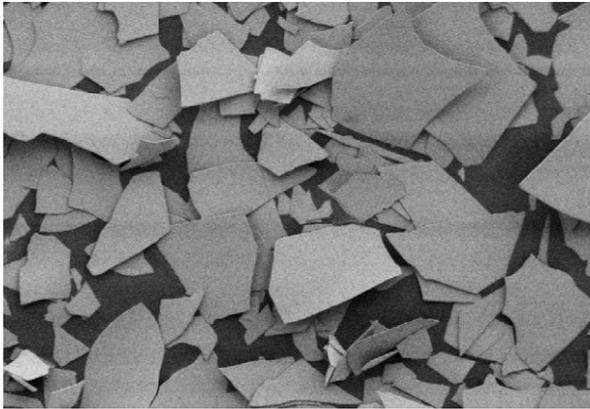
**Figure 1:** Scanning Electron Micrograph of a fused toner image containing leafing type metallic flakes

The use of metal or metal oxides flakes has been described in the literature for their use as metallic pigment in toner applications [3]. In addition to the various drawbacks described previously, the use of some metal powders also poses severe safety hazards. Many of the metal oxide powders are quite suitable when non-contact fusing methods are used. These metal flakes are typically treated with various low surface energy organic coatings which allow flakes to migrate to the surface upon heating and leaf them together

as shown in Figure 1. However, charge concerns still remain with such formulations.

In order to avoid the difficulties associated with electrical conductivities, pigment flakes based on mica, alumina and silica have been described in several toner applications [4-6]. Several other flat surfaces have also been disclosed as potential pigments for toner capable of producing metallic effects [7, 8]

The metallic effect also heavily dependent on the size of the pigment flakes employed. As the diameter of the pigment flake increases, the resulting metallic effect or “sparkle” of the image also increases. The metal flakes that are used in automobile paints exceed 500 microns and can often be in millimeter size range. It would be impossible to incorporate such larger pigments in typical toners. Over the years, the size of the toners has been shrinking down because of image quality and cost reasons. The desire to produce toners with metallic appearance is clearly at cross-roads with the image quality considerations.



**Figure 2:** Scanning Electron Micrograph of treated mica flakes useful as pigment for metallic toners.

As the size of the toner is increased, the mass of the toner increases at a much accelerated cubic rate. A toner which is 3 times larger also has 27 times more mass. When particles are much larger, one of the major difficulties that is encountered is the fixability of the toner image because of the higher mass and stack height. The mass of the toner would also be higher because of the specific gravity of the pigment flakes useful for this application. Typically the pigment flakes have specific gravity that is about 3 to 4 times higher and thus places extra burden on the already higher mass with larger toner size. Also, the thermal conductivity of the additive can also play an important role in the ease of fixing such toners.

### Preparation of Metallic Toners

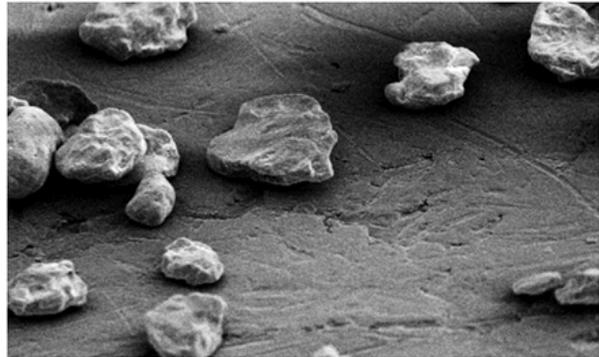
The selection of the pigment flakes is one of the most important considerations for the development of metallic toners. During the development of such metallic toners, it was found that metallic sparkle or metallic flop was dependent on the size of the pigment flake that could be incorporated in the toner. Most benefit is derived from using as large a pigment flake as possible that can be incorporated in the desired toner size. Pigment flake particles that are less than 5 microns were found not be as effective as the

larger pigment particles. The other consideration is the electrical conductivity of the pigment flake. Most metal flakes have high electrical conductivity that leads to deterioration of electrical charge. For this purpose coated mica particles, as shown in Figure 2 were utilized. These particles have high aspect ratio and are about 1 micron thick. Depending on the number and thickness of high refractive index material over mica flakes, different color effect can be produced. These types of interference pigments are available from various sources including BASF, Merck/EMD, and Sun Chemicals.

In order to produce toners that are capable of providing the maximum sparkle or metallic effect, it is important to keep size of the pigment flake as large as possible. Typically these flakes are very fragile and can fracture very easily. To minimize the breakage of the pigment flakes during the toner manufacturing process, the inherent shear forces need to be kept as low as possible. This was achieved by appropriate optimization of:

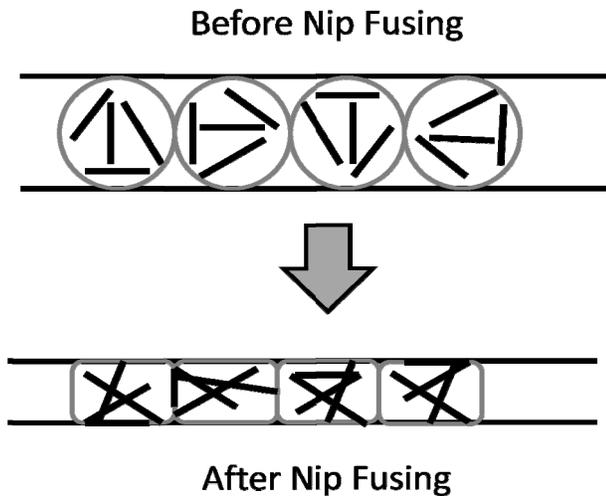
- processing temperature
- extruder screw configuration
- throughput rate
- molecular weight of the polymer resin
- shear thinning additives

In addition, the exit geometry of the die was modified so as to cause a convergence in the melt slab. Additionally, the draw ratio of 2 or higher was applied to the strands following the exit from the die face to further intensify the orientation of the pigment flakes. When toners were prepared by pulverization process, the resulting toner particles were found to have a very pronounced flat shape. Example of the flat shape of such toner particles is shown in Figure 3.



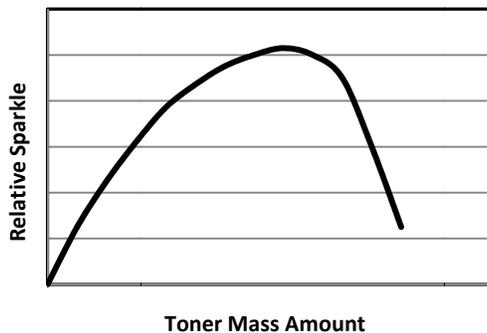
**Figure 3:** Scanning Electron Micrograph of toner particles suitable for producing metallic effect

In order to increase metallic effect, it is necessary that the reflecting planes of the pigment flakes are parallel to the plane of the paper or any other substrate used. When toner mass laydown is high, the toner particles and surrounded by other toner particles in every direction. The toner melt under the fusing conditions is essentially an incompressible fluid. As this toner mass goes though the fusing nip, there is almost no realignment of the pigment flake possible. This results in a reduced sparkle effect.



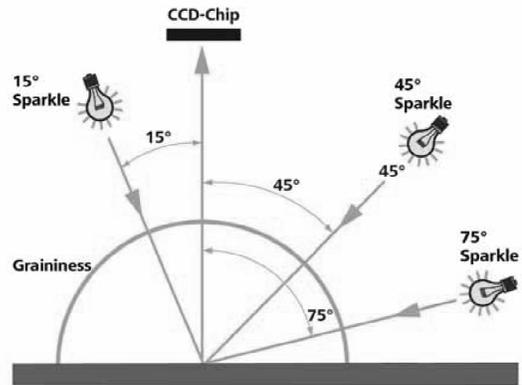
**Figure 4:** A schematic representation of restricted lateral flow on toner melt at high toner mass.

A schematic representation of this absence of flow in incompressible toner melt and the resulting lack of orientation of pigment flakes is demonstrated in Figure 4. At lower toner mass amount, there is an increase in the lateral flow, which is similar to a dot gain during the fusing process. Because of this spreading, more sparkle can now be observed at lower density. This relationship between the observed sparkle and the toner mass amount is shown in Figure 5. When there is sufficient connectivity among the pigment flakes in the plane of the paper substrate, highest sparkle effect is observed. Beyond this toner mass, the spreading is impeded and thus images with reduced metallic effects are produced.



**Figure 5:** Relationship between the relative sparkle in the image and toner mass laydown.

When such toners are transferred to the paper surface, the pigment particles were mostly aligned in the plane of the paper. This results in increased sparkle and the generation of the desired metallic effects. The metallic effect can be produced either directly on the substrate or these metallic effect toners could be placed over or under other colors to produce myriads of special digital effects.



**Figure 6:** Configurations used in instruments to measure sparkle in images produced with metallic toners.

Measurement of metallic effect has its own challenges. The amount of sparkle in an image changes with observer, light sources and the observation angle. In order to quantify the metallic effect in an image, changes in the reflected light intensity are measured at various angles as shown in Figure 6 and used to determine Flop Index. The Flop Index [9] is the measurement of the change in reflectance of a metallic color as it is rotated through the range of viewing angles. A flop index of 0 indicates a solid color, while a very high flop metallic basecoat color may have a flop index of 15–17. Flop Index is mathematically defined by:

$$\text{Flop Index} = \frac{2.69(L_{15^\circ}^* - L_{110^\circ}^*)^{1.11}}{(L_{45^\circ}^*)^{0.86}} \quad (1)$$

With conventional toners the toner is ground down to a smaller size, hence is somewhat possible to prepare toners is large metallic pigments. However, the methodology currently used to produce most Chemically Prepared Toners will have a tpuher time to produce such metallic toners. It is believed that since very small particles are “grown” in CPT processes to the desired final larger toner size, it would be much harder to produce metallic toners due to the inability to incorporate larger pigment flakes.

## Conclusions

It is possible to produce electrophotographic toner that are capable of exhibiting sparkle and various metallic appearance to prints. In order to accomplish this, interference pigments were used to produce metallic toner and overcome the electrical issues that are encountered with metal flakes. By optimizing the manufacturing conditions such that the breakage of the fragile pigment flakes is minimized, toner particles were produced which have a flat shape. These toners exhibit metallic effects when fused on the substrate directly or over/under other color toners to produce prints that exhibit different metallic color effects. The toner mass laydown amount was found to be an important factor as very high toner amount prevents spreading of the toner which is necessary for producing metallic effects. Further, the pigment flake concentration was also found to be an important parameter since it can affect the melt viscosity and the shear conditions experienced

during the manufacturing process. The image fixing can also be adversely affected as the pigment concentration is raised.

## References

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## Author Biography

*Dinesh Tyagi received his Ph.D. degree from Virginia Tech in 1985 from the Department of Chemical Engineering with a thesis entitled "Structure-Property Relationships in Segmented Polymers." After one year of post-doctoral position there, he joined Eastman Kodak Company as a Research Scientist where he specializes in the field of digital printing and polymer research. He was promoted to Senior Research Scientist in 1989 and in 1993 he was appointed Research Associate. The following year he was inducted into Kodak's Distinguished Inventors Gallery. In 1999 he joined NexPress Solutions, which later became part of Kodak. He has continued to work in the area of toners and electrophotography through most his professional career. Dr. Tyagi has over 100 patents worldwide. In 2011 Dr. Tyagi was awarded Chester F. Carlson Award for his innovations and broad contributions to electrophotographic toner technology.*