The Anatomy of a Toner

Toner is a very familiar material to most people who have worked in the printer and copier industries, as well as to anyone who has worked in a business no matter how large or small. With the exception of some specialized toners used in large-scale commercial print applications, the modern day toner is a powder that has the consistency and fineness of wheat or corn flour. Most people in the past have been familiar with black toner but nowadays, colored toners are becoming more and more common in the workplace. Before color, many people imagined that the black toner was just like soot from a chimney or flue. After all, the close encounter most average people have had with toner has left them with messy black powder on their hands and their clothes just like soot. Of course this is far from the truth when looking at the composition of a black toner and of course colored toners. Toners are, in fact, very complex mixtures of a variety of raw materials all with their own specific function in the hard copy creation process.

What Toner Parameters Affect Which Part of the Process?

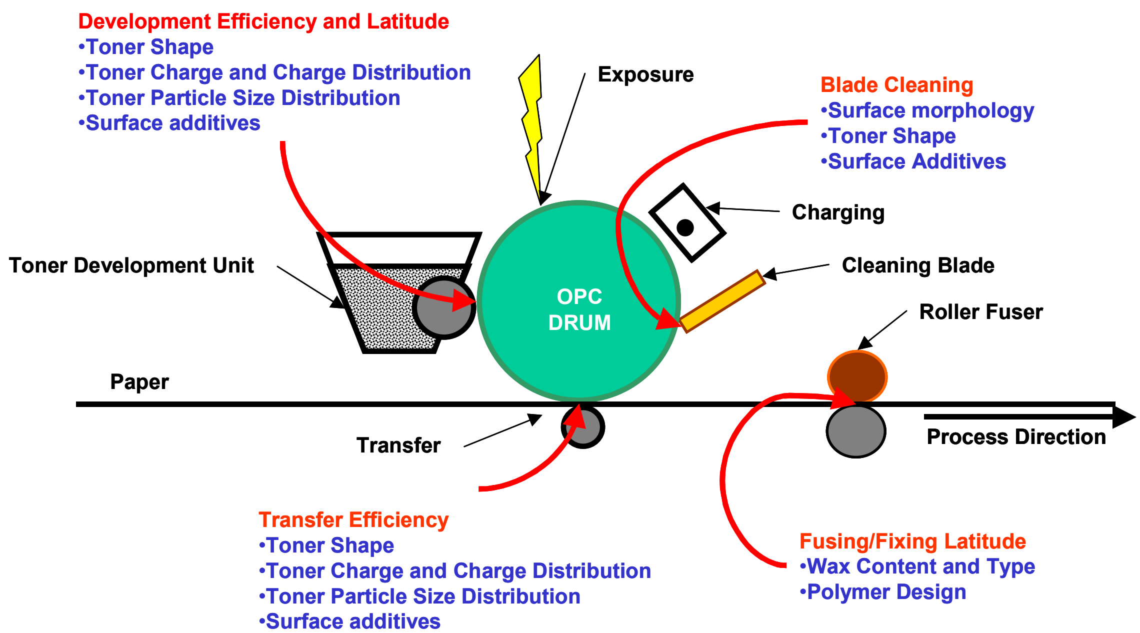
Toner based print engines comprise a number of subsystems – charging, imaging, developing, transfer, fusing/fixing and cleaning. Each subsystem has critical requirements of the toner. Some of the critical parameters conflict with those required by the other subsystems. For example, high levels of internal wax desirable for release in fusing/fixing conflict with the requirement for minimization of wax content for high flowability needed for good development and transfer. Similarly, spherical toner particle shape is best for high transfer efficiency but this is completely counter to the need for irregular shape and high coefficient of friction between the cleaning blade and the photoconductor for the most efficient cleaning with a cleaning blade. Inevitably in toner design there are trade offs between the different requirements and toner performance overall.

In toner formulation and manufacturing there are many parameters that can be manipulated. The ability to manipulate these parameters depends upon the materials, the manufacturing equipment and the toner technology used to make the toner. Variable parameters of any toner include:

Toner Particle Shape
Toner Charge
Toner Charge Distribution
Toner Particle Size Distribution
Surface additives
Wax Content and Wax Type
Polymer Design
Surface morphology
Charge Control Agents

The diagram below illustrates the impact of some of the poarameters in toner on the print subsystems and processes in printing.

Toner Design Parameters and the Print Process Steps



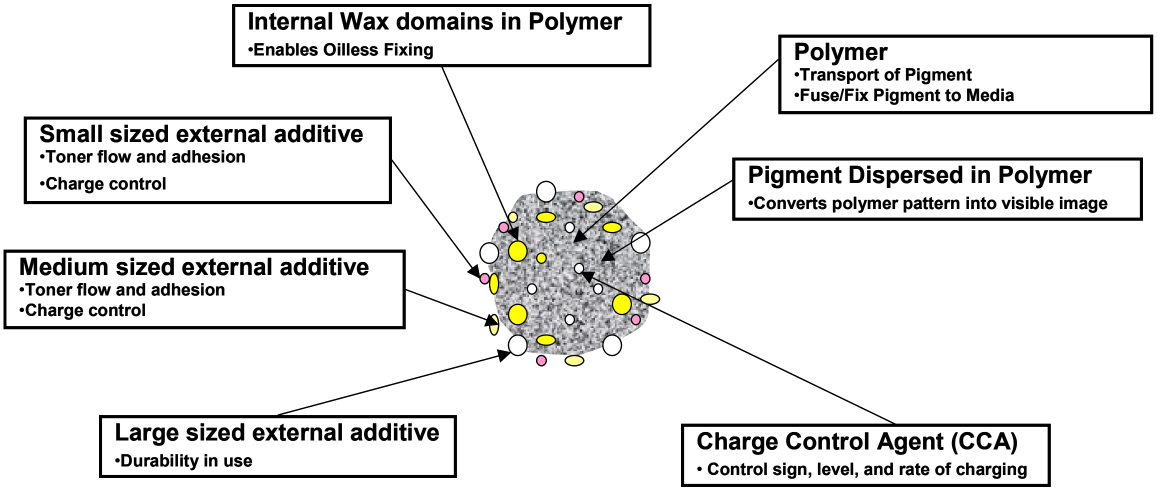
Toner Composition

When thinking of powder or dry toners, there are three basic categories into which all such toners fit. There are:

- Mono component magnetic toners
- Mono component non-magnetic toners
  and
- Dual Component toners

Despite these different categories, which are based upon the type of image development process used in the engine, all powder toners have common elements to their composition. All powder toners contain a polymeric resin, a colorant and for many years now, but not in the beginning, additives having a variety functions.

Schematically a modern toner can be represented diagrammatically as shown in the diagram below:



The actual toner composition varies not only by toner type, but also from toner to toner for different engines. A general formulation for each of the different types of toner is shown in the table following:

	Monochrome	Monochrome	Color
Toner Type	dual component or mono component non - magnetic	mono component magnetic)	dual component or mono component non - magnetic
Binder Polymer(s)	70 - 90%	40 - 65%	85 - 95%
Iron oxide	0 - 15%	30 - 50%	0%
Dye/pigment	0 - 6%	0 - 6%	1 - 8%
Release agent	0 - 4%	0 - 6%	0 - 2%
Bulk CCA	0 - 4%	0 - 4%	0 - 2%
Flow agent	0.1 - 3.0%	0.1 - 3.0%	0.1 - 4.0%

The Polymer

This is the ingredient of toner that represents the major proportion of any toner composition. Dependent upon type, the polymer is present as between 40 and 95% of the toner composition. The function of the polymer is to act as a “binder” or vehicle to carry the colorant and hold the colorant against removal on the final printed page. There are various requirements of the polymer sometimes called the toner binder. The melting characteristics of the polymer are vitally important. It must be thermoplastic, in other words it must be deformable by the application of heat and in most cases the toner binder must fluidize to the right degree when heated beyond its’ melting point. The polymer is chosen such that the toner will have the correct fusing matching the fuser in the print engine..

The choices that have to be made in selecting the correct toner binder are of the chemical nature and molecular weight. The commonly used types of toner binder are:

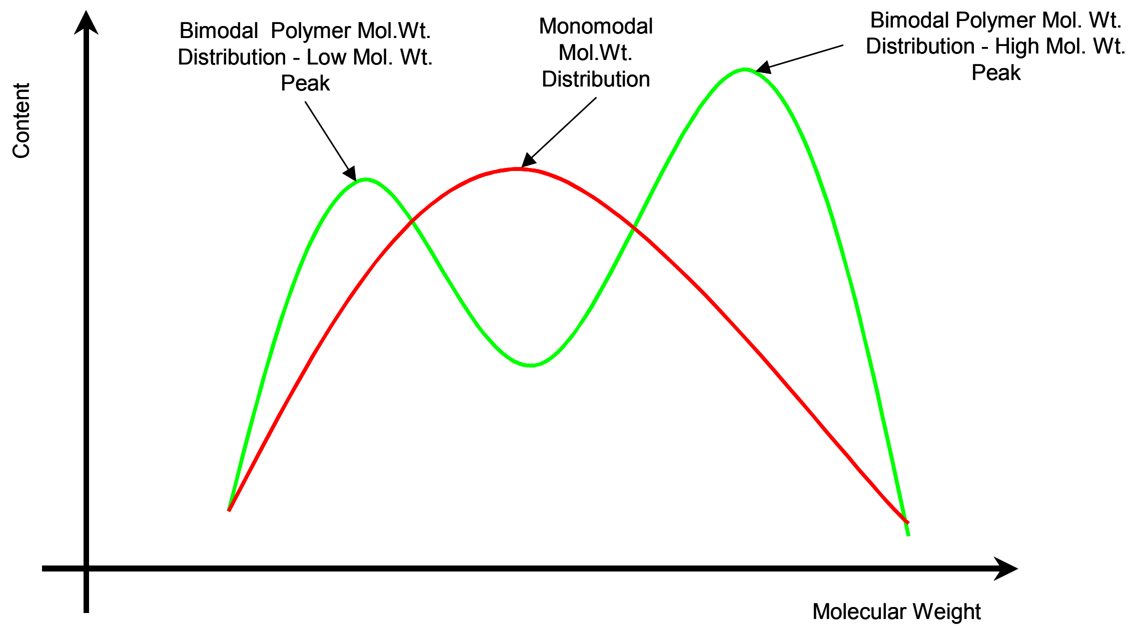
Styrene Copolymers of Acrylic Resins e.g. Styrene PolyMethyl Methacrylate
Styrene Copolymers of Butadiene
Polyesters

Typically these polymers are amorphous polymers and have a Glass Transition Temperature (Tg) of 50 -70 ºC. Tg is usually determined by the chemical composition, polymer structure and the molecular weight distribution of the polymer. These parameters directly affect the processing manufacturability of the toner formulation, the stability of the resultant toner in storage and use, the print gloss level and the quality of the fixing/fusing step in the print process.

High molecular weight polymers tend to have a high melt viscosity and when used as a toner binder result in a toner with a high fusing temp. The resultant compound of the raw materials from which the toner is manufactured tends to be tough and slow in manufacturing throughput rate. On the other hand, low molecular weight polymer tend to be brittle and offsets onto the fuser rolls under the wrong conditions. It may also make a toner subject to poor storage life because of toner “blocking” (tackiness in storage) even under normal ambient conditions.

The rheology or complex viscosity of the toner formulation in the melt stage in fusing/fixing is largely determined by the polymer characteristics. Some polyesters for example are simple polyesters with very sharp melt viscosity characteristics that provide the opportunity to achieve very high gloss. On the other hand some polyesters are implemented with a great degree of cross-linking that changes the melt flow of the resin giving better fuser latitude, but reducing the print gloss. The molecular weight distribution controls the minimum fixing temperature and the toner resistance to defects known as cold offset and hot offset. The resin of course has to be chemically compatible with the other ingredients of the toner. As a major constituent of the toner, the polymer plays a major role in determining the cost of the toner from the raw material and the producability standpoints.

Blending high and low molecular weight, or cross-linking part of the polymer enables the achievement of low melt temperature and wide fusing latitude. This can be done to such an extent that the resulting polymer has a distinctly bimodal or double peaked molecular weight distribution. The chart below shows the comparison of a mono modal (single peak) and a bimodal or double peaked molecular weight distribution. The lower molecular weight fractions of the toner binder are responsible for the initial melt of the polymer matrix and the consequential adhesion of the toner to the medium being printed. The higher molecular weight fraction is responsible for the resistance to offset in the fuser system and resistance to scratching and cracking of the printed item.



When considering the different types of polymer used, in general, polyesters have the advantages of giving the toner a lower minimum fix temperature while maintaining a higher Tg. Polyesters however tend to be more expensive than the other candidate polymers. Styrene/Acrylic copolymers have the advantages of not only lower material cost but also higher throughput toner production rates providing further economic advantage. These copolymers also tend to be lower in humidity sensitivity and this translates into more robust performance in a variety of environmental conditions.

Clearly there are advantages of the use of Polyester and of Styrene/Acrylic Copolymers. There are continuing attempts to try to get the best of both worlds by the use of hybrid polymers. Such hybrids fall into the categories of polyaddition of vinyl monomers with unsaturated polyesters and polycondensation of diols and diacids with functionalized polyolefin as well as mechanical methods of combining the different resins by co-agglomeration and melt mixing.

The Pigment

The two categories of colorants are available to the toner formulator are pigments and dyes. Pigments predominate in usage in toners because of their better stability and resistance properties. Pigments are colored, black, white, or fluorescent and are particulate organic and inorganic solids that are usually insoluble, and essentially physically and chemically unaffected by the toner polymer or media in which they are incorporated.

The Key Properties of pigments for use in toners are:

Good Dispersion
High Color Strength and Purity
Good Light Fastness
Good Colored Pigment Transparency
Chemical Suitability for High Pigment Loading
Correct Triboelectric Charging Characteristics
Non-Toxic and Safe in Manufacturing and Application

Black Toner Pigments

The most common pigment type used in toner is carbon black. This very common pigment is used in all manner of products from tires to plastics to paint. Competing raw materials are dyes, and other organic/inorganic materials. Carbon black is used in two component and mono component non-magnetic toners and, to a lesser extent, in mono component magnetic toner materials. In two component toners and mono component non-magnetic toners the level of inclusion can be from 4 to 8 % by weight though some toners contain up to 15%. In mono component magnetic toner the level is much lower being normally less than 5%. In the latter the coloration is largely a role of the high percentage of iron oxide or magnetite incorporated in such products. Carbon black is used because in comparison to other black colorants it exhibits excellent heat and light fastness as well as good price performance characteristics.

The use of special carbon blacks in toners is not uncommon. Carbon by nature is an electron donor. Oxidation of the surface of a carbon black particle increases the level of carboxyl and carboxylic acid groups on the surface. This changes the material surface from that of an electron donor to electron acceptor. This improves the carbon blacks ability to hold negative charge. This property is of course imparted to a material such as toner into which the material is compounded. Carbon black pigments surface treated by oxidation are products popular with the toner formulator. This type of treatment imparts improvement in dispersion and in negative tribo electric charging characteristics. The best grades of carbon black for this purpose tend to be smaller in particle size and thus though higher in color strength more difficult to disperse and browner in shade.

The important properties of carbon blacks for the toner formulator are:

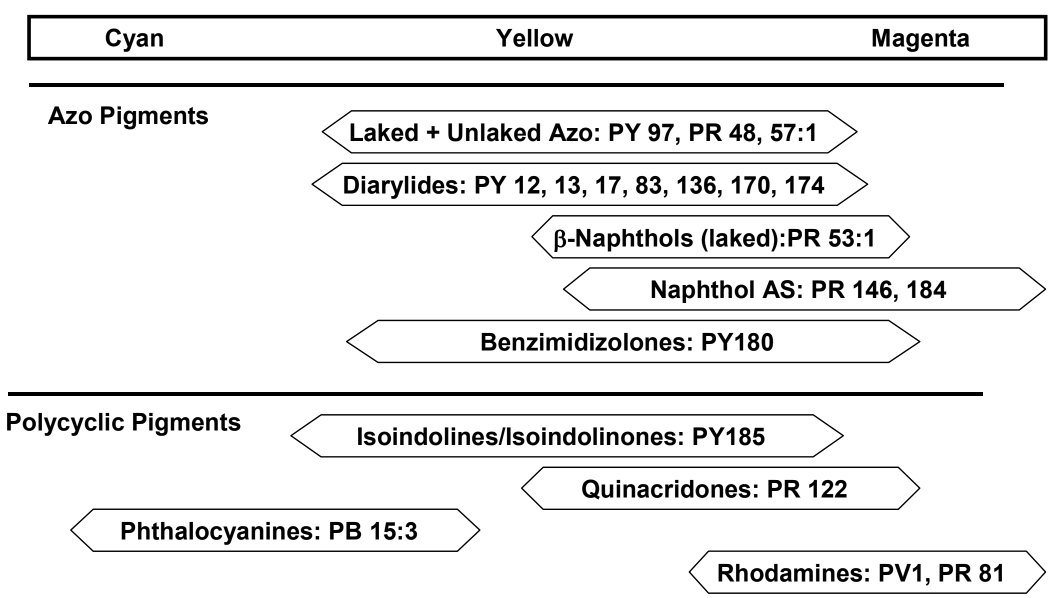
- Ease of dispersion
- Particle size
- Acid value (a determinant of charging behavior)
- Jetness

- Handleability
- Ames Negative

The particle size of the carbon black has an affect on its dispersibility. The smaller the particle size of the carbon black the more difficult or slower the dispersion will be. Good control of dispersion requires that the rate of dispersion for a carbon black be at a level where this is not too fast as this hampers good control of the degree of dispersion. Different grades of carbon black are available – fluffy or beaded grades. Fluffy carbon blacks can be slower in their dispersion than beaded grades and can therefore be subject to unpredictability in production for homogeneity and dispersion. The particle size of the pigment can be from 0.01 to 0.5mm

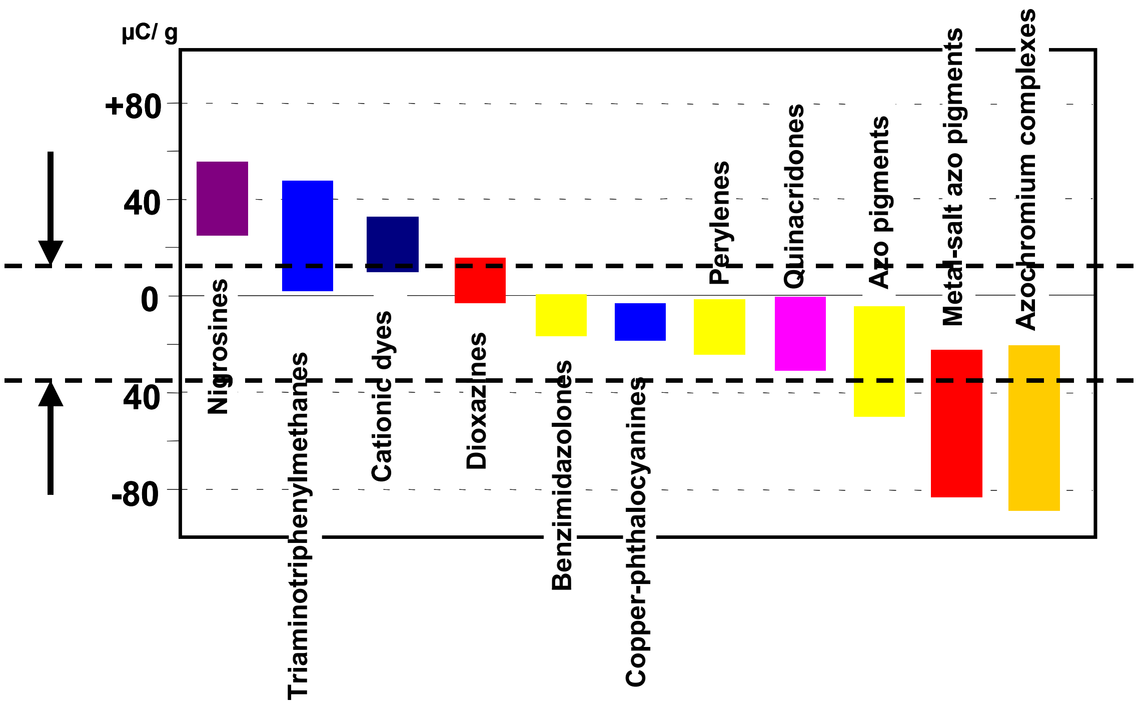
Colored Toner Pigments

There are two primary categories of pigments to choose from for colored toners – Azo and Polycyclic pigments. These categories span the spectrum of colors required for the production of all colors. For a "process set" of colors for color printers we need to choose appropriate pigments to make Magenta, Cyan and Yellow toners in addition to Black. With the appropriately formulated four toners it is possible to print a wide gamut of colors by their combination in particular degrees of overlap. The chart below adapted from data produced by Drs. Macholdt and Bauer of Clariant shows the range of pigments available to the formulator:



The pigment loading depends upon the color of the toner and hence pigment choice made. Typically the pigment content is from 4 to 20%. For cyan toners the typical choice of pigment is copper phthalocyanine (Pigment Blue 15:3). This latter descriptor is the Pigment Index category for the pigment. Similarly for magenta toner the typical choice is a quinacridone pigment (Pigment Red 122). A variety of pigments are available for yellow toners. The pigments are Azo pigments and a common choice is Benzimidizolone (Pigment Yellow 180.)

One factor of importance to the toner formulator is the affect of the pigment chemistry on the triboelectric charging of the toner. Chemically different pigments and therefore different colored toners can charge differently. The objective in formulating a colored toner set is to make the toners behave similarly in charging. The next illustration shows the difference in charging behavior between different types of pigment. The diagram shows the typical charging level, range and sign of charge developed when contacting a standard metal surface and the resulting charge is reported in microcoulombs per gram.



The choice of pigments is thus not trivial, but toner charging of course is a function of the overall toner composition and charge control agents may be used to overcome the inherent behavior of the pigments.

Iron Oxide Pigment / Magnetite

Many toners incorporate the use of iron oxide pigment or magnetite that are submicron in size. Iron oxide is included in large proportion in magnetic mono component toners and is included to about 30 – 40% in such toners. Magnetite is also used in some dual component toners but for a different reason than in magnetic mono component toners. The latter type of toner is used on its own as a single element in the development system. The development unit has at its heart a magnetic development sleeve and the iron oxide in the toner imparts intrinsic ferro magnetic characteristic in the toner needed for the toner to be transported to the development zone by this sleeve. In the dual component system, the toner is mixed with a ferro magnetic carrier that transports it to the development zone by way of a magnetic developer sleeve. The Iron oxide in the toner is to prevent dusting and aid in cleaning.

Internal Charge Control Agent

Internal charge control agents perform a number of functions in toner. They control the sign (positive or negative) of charge developed. They control the saturation charge magnitude, the rate of charging and the stability of charging of the toner. As previously mentioned they can be used to adjust the charge level for different pigments in the different colored toners.

Key Properties of charge control agents are compatibility with the polymer and the ability to create uniformity dispersion. Typical CCAs are salts composed of small labile ions and much larger counter-ions. These can be positive or negative charging CCAs. An example of a positive CCA is nigrosine or Quaternary Ammonium Salt and a typical negative CCA is a metal-dye complex. The important characteristics of CCAs are the CCA surface in its polarity, net charge intensity and donor/acceptor nature. The bulk properties of the CCA in crystallinity and dielectric properties are also important to toner charging. Underlying these factors is the chemical nature of the CCA. There are a number of theories as to the mechanism of tribo electric charging. So far there is no definitive theory for the CCA charging mechanism, but there is much experimental data and experience linking these factors to the charging behavior of toner including CCAs.

Surface Additives

There are a number of materials that are used as surface additives for toners. They are used to impart a variety of properties to the toner material. They include the following:

Fumed Silica
Metal Stearates e.g. Zinc Stearate
Fluoropolymer powders
Magnetite
Cerium Oxide
Carbon Black

The reasons for the inclusion of these additives include improvements to the following areas:

Flow Control	(e.g. Fumed Silica)
Charge Control	(e.g. Fumed Silica)
Cleaning	(e.g. Cerium Oxide)
Cleaning Blade Lubrication	(e.g. Zinc Stearate)
Conductivity Control	(e.g. Carbon Black)

These materials are normally incorporated as finely divided powders and are blended with the toner by dry blending. More than one material may be used in a toner formulation. Clearly the properties of the additive material control specific toner properties and it is important that there is no adverse interaction between two or more additives or additive and component.

Silicas (Fumed or Pyrogenic Silicon Dioxide) are primarily used as powder flow promoters. They are used in all types of powder toners dual component, and mono-component, both magnetic and non-magnetic. Flow is a critical property of powder toner affecting a variety of functions in the print process including delivery of toner from hoppers and cartridges and the admixing process. Silica also has the affect of helping to prevent coalescence/blocking of toner in storage and in use.

In addition to the action of promoting flow and to some extent preventing coalescence of toner particles, silicas improve the transfer properties of toners in printing by lowering the magnitude of adhesive forces between the toner and the photoconductor. Furthermore, they are also used to help control the charging and stabilize the charging of toners. The amounts incorporated vary according to the application and are normally in the range of 0.1 to 2.5% by weight of ground and classified toner.

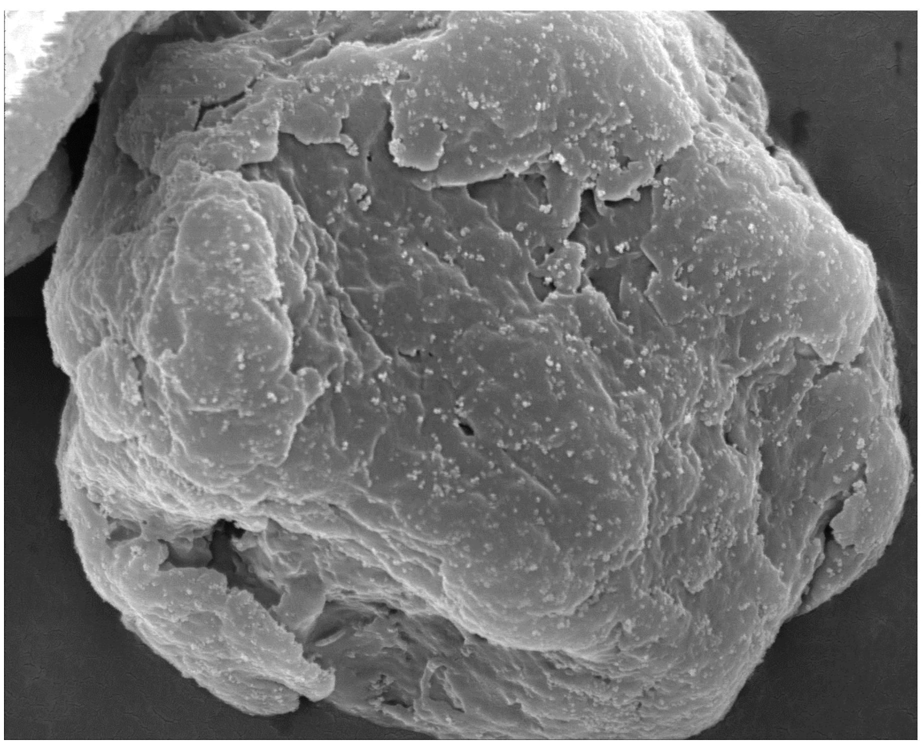
There is much use of silicas as negative charge control agents. The natural negative charging tendencies of silicas have resulted in some formulation difficulties where toner of positive charging type is to be formulated. In both negative and positive toner applications, the addition of an adequate amount of silica to promote flow is necessary. Special positive charging types, treated with amongst other materials aminosilanes and hexamethyldisilazane to impart some degree of hydrophobicity, are now available for positive toner applications. Negative charging silicas are normally types treated for hydrophobicity.

Different size silicas have different properties and purpose as surface additives. Small size silica < 20 nm has significant affect on powder flow of the toner. The us of small size silica leads to lower cohesion between toner particles resulting in better flow at the same fractional area coverage as larger silicas. However, small silicas lose their influence on flow properties more quickly than larger silicas. Medium size silica > 20 & < 100 nm helps to minimize adhesion forces between the toner and any surface such as a photoconductor surface enhancing transfer efficiency. Large size silica > 100 nm improves the durability, by preventing embedding and loss of smaller silicas from the toner surface. For example typically 150 nm silica at about 27% surface coverage preserves transfer efficiency much better than 40 nm silica alone. Key properties of silica are the tribo-electric characteristics, the hydrophobicity and ease of dispersion. Most silicas used in toners have hydrophobic treatments that affect charging and flow properties. These treatments include Dimethyldichlorosilane (DMDC), hexamethyldisilazane (HMDS), polydimethylsiloxane (PDMS), alkylsilane for negative charging. Some positive types are treated with aminopropylsilane (APS).

Fumed Alumina is less commonly used as a surface additive in toners than silica. Its affect on the flow properties of toner is less marked. The properties of Aluminium Oxide show that there is a marked positive charging tendency in some systems. Fumed or Pyrogenic Titanium Dioxide, like Alumina, has found much less common usage as an external additive than silica. It is used as an alternative flow and charge control aid.

Fumed or Pyrogenic Titanium Dioxide is slightly positive charging and is commonly treated with alkylsilane as a hydrophobicity treatment.

In the SEM below the difference in the scale of size between the silica and the toner can be clearly seen. This dual component toner particle is about 8.5 microns in diameter. The small white particles on the surface of the toner are silica particles.



Other Ingredients

For many years now toner formulators have included wax in toner to improve release properties of the molten toner from the fuser rolls. Typically, polypropylene waxes have been used for this purpose in black toners but there is increasing usage of lower molecular weight polyethylene and polypropylene waxes as methods of enabling oil less fusing. In addition to this improvement in fixing/fusing, waxes also prevent smearing in automatic check readers in MICR toner applications. These waxes are solid at room temperature, but much reach a lower viscosity than the toner polymer in fixing/fusing step of the print process. Incorporation of the wax into a toner, particularly conventional melt mixed/compounded types is difficult because of the different temperature-viscosity relationship compared to the toner resin. The right degree of dispersion of wax must be achieved because poor dispersion can lead to flow and adhesion problems. More recently, ester waxes have started to be used by the toner formulator for their better properties. In particular this has been important in colored toners that require a high degree of transparency and where a higher concentration of wax is common.

Toners are complex materials that are formulated to highly exact tolerances in composition and physical form. There will continue to be much research into improvements in toner design as expectations of print performance continue to be refined.