AEROSIL® Fumed Silica and AEROXIDE® Oxides for Toner

Technical Information TI 1222

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1 Introduction

Evonik Industries is the world's leading supplier of fumed silica and fumed metal oxides for the digital imaging industry. With the ever increasing diversity of requirements and technical complexity of today's toner industry, we have developed a broad line-up of AEROSIL® and AEROXIDE® additives. This technical information brochure presents the properties and performance attributes of our fumed silica and metal oxide based toner additives. It is an aid to the toner formulator seeking to employ Evonik´s quality and technical creativity to meet the challenges of the global toner industry.

1.1 Overview

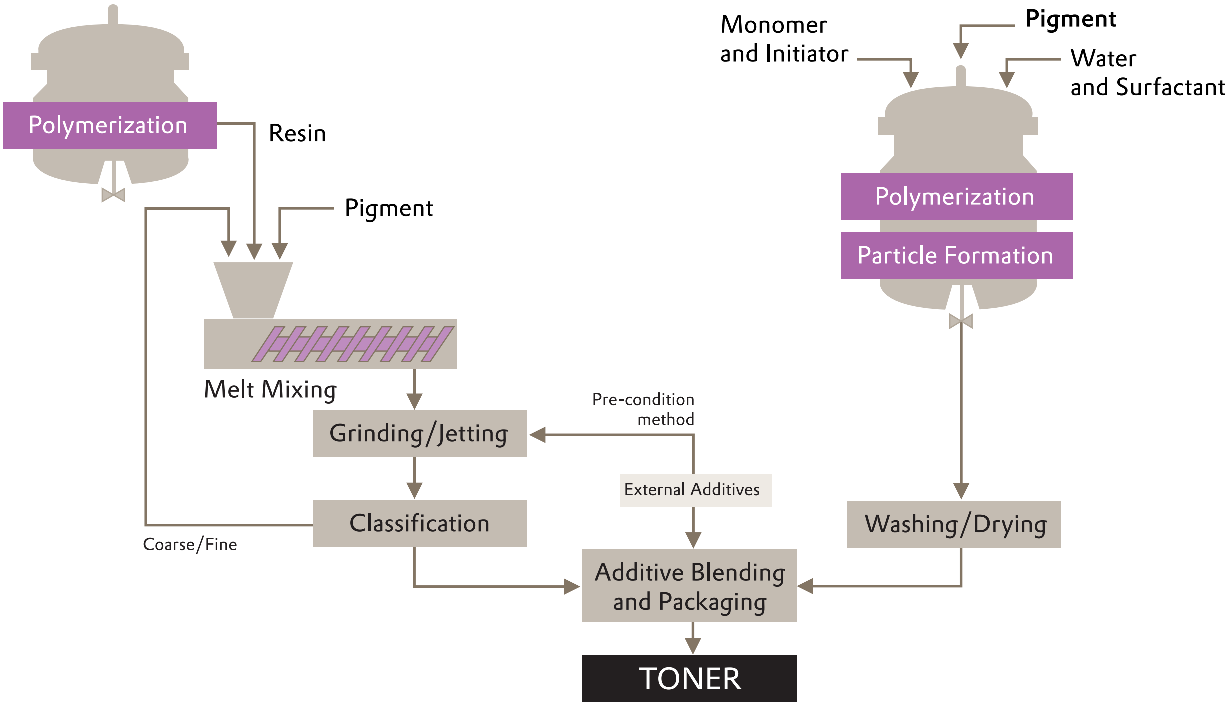
The electro-photographic process, also referred to as xerography, was invented by Chester Carlson in 1938.
It involves the creation of a visible image from an electrostatic latent image. The electrostatic image in the form of surface charge patterns on a photoconductive surface – the so called photoreceptor – is developed using charged toner particles which are transferred and fused to the paper surface. The first commercial xerographic copier, the Xerox 914, made seven 9"×14" copies per minute in black. Current copiers, high speed color laser printers, and digital presses print up to 100 pages per minute in full color.

Conventional mechanical toners are produced by mixing and usually extruding a pigment/thermoplastic resin mixture. The extrudates are then pulverized (crushed/milled) and the desired particle size fraction is blended with external additives particularly to adjust powder flow and tribo-charge.

Chemically produced toners (CPT) are manufactured from water- and/or solvent based emulsions or suspensions of monomers which are polymerized in the presence of a colorant. Like mechanical toners, they are subsequently blended with external additives (**Figure 1**).

The basics of toner formulation consist of: pigment, resin, wax, and, most often, charge control agent(s). Of course, the proper choice of pigment is an essential first step. However, each of the other ingredients plays a critical supporting role. The polymer of the toner particle is chosen so that the toner will tribo-electrically charge to the preferred polarity and melt at the desired fusing temperature. Internal waxes are added to lower toner adhesion to the fuser roll and improve toner fixation to the paper, and charge control agents (CCA) are added to control the sign, level, and rate of tribo-charging.

Figure 1 Schematic depiction of mechanical (**left**) versus chemical toner processing (**right**)[1,2]



2 Manufacture and Properties

These are the basics of design for a toner particle, but for the electro-photographic process to work reliably and produce the highest quality image, so-called external additives have been developed. The most commonly used external additives are silica and/or metal oxide particles that adhere to the toner surface. Evonik surface-treated AEROSIL® fumed silica (SiO_2) and AEROXIDE® fumed metal oxides (Al_2O_3, TiO_2) are highly efficient external additives for mechanical and chemical toner that:

- Greatly enhance powder flow
- Minimize or even eliminate image background problems
- Reduce sensitivity to relative humidity and greatly improve storage and moisture stability
- Allow precise tribo-charging and avoid slow admix
- Enable easy cleaning of photo-conductor drums

In essence, the toner surface takes on the characteristics of the silica and/or metal oxide. In this way it is possible to control the properties of the toner in a well-defined manner by selecting the right combination of AEROSIL® and AEROXIDE® external additives.

The Evonik manufacturing process for AEROSIL® fumed silica and AEROXIDE® fumed metal oxide based external additives typically consists of three fundamental steps:

1 core particle synthesis,
2 surface modification, and
3 structure modification

The combination of these steps (**Figure 2**), which can be carried out continuously or batch wise, allows the precise and tailor-made design and synthesis of external additives fulfilling the most stringent requirements of today's toner formulations.

Figure 2 Fundamental process steps for the manufacture of AEROSIL® and AEROXIDE® external additives and their impact on and application properties in toner

	Core Particle Synthesis	Surface Modification	Structure Modification
Product Properties	Core Composition	Hydrophobic Groups	Aggregate Size
	SiO_2	Dimethylsilyl-	
	Al_2O_3	Trimethylsilyl-	Agglomerate Size
	TiO_2	Polysiloxane	
	Special Particles	Alkylsilyl-	
	$SiO_2/TiO_2/Al_2O_3$	Functional Groups	
	BET Surface Area	Aminoalkylsilyl-	
	50–380 m^2/g	Group Combinations	
Application Properties	Flow Enhancement	Hydrophobicity	Dispersibility
	Tribo-charging	Flow Enhancement	Processability
	Stability	Tribo-charging	
	Durability	Stability	
		Dispersibility	

2.1 Core Particle Synthesis

AEROSIL® fumed silica is a synthetic amorphous silica manufactured by hydrolysis of chlorosilanes in an oxygen-hydrogen gas flame according to the reaction:

$$SiCl_4 + 2H_2 + O_2 \longrightarrow SiO_2 + 4\,HCl$$

The manufacturing process was developed by Evonik´s predecessor company Degussa in 1942 and has continuously evolved in scale and refinement since then. Because AEROSIL® fumed silica is produced by flame hydrolysis, it is referred to as fumed silica.

Metal oxides, such as aluminum oxide (alumina) and titanium dioxide (titania) can also be produced using the AEROSIL® process. Evonik markets these metal oxides under the trade name AEROXIDE®. The reaction equation for alumina, for example, is as follows:

$$2\,AlCl_3 + 3\,H_2 + 1.5\,O_2 \longrightarrow Al_2O_3 + 6\,HCl$$

Evonik also produces various mixed oxides such as our Fumed Silicon-Titanium Mixed Oxides. Their structures largely depend on the ratio between TiO_2 and SiO_2.
AEROXIDE® STX 801, for example, consists of a titanium dioxide core and a silica shell.

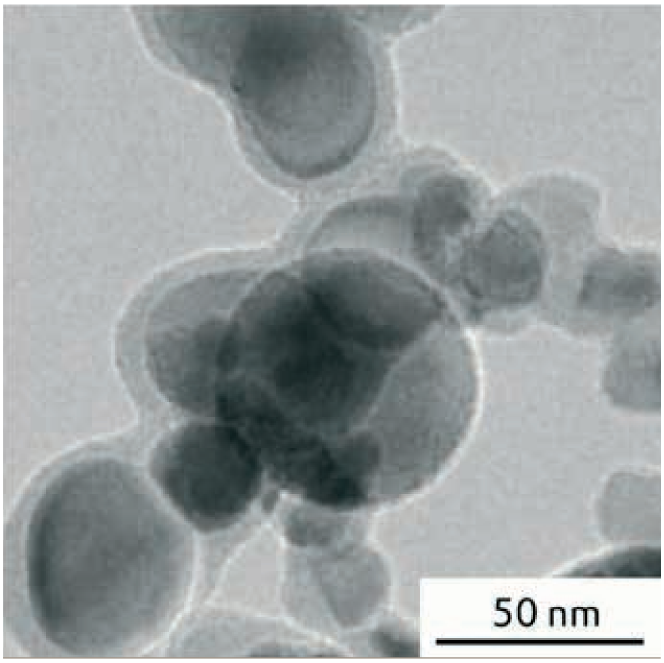


Figure 3
Transmission Electron Microscopic image of a fumed Silicon-Titanium Mixed Oxide with a silica shell and a titanium dioxide core

The tribo-charging properties of an external additive are first and foremost determined by the electrical resistance of the base metal oxide itself (cf. **Table 1**). Consequently, the tribocharge of our products becomes increasingly more negative in the following order:
AEROXIDE® fumed alumina < AEROXIDE® fumed titanium dioxide < AEROXIDE® fumed silicon/titanium mixed oxides << AEROSIL® fumed silica.

Table 1 Basic physical properties of silica, alumina, and titanium dioxide

	Unit	SiO_2	TiO_2	Al_2O_3
Specific gravity	g cm^{-3}	2.2	3.8	3.3
Refractive index	–	1.46	2.5	1.7
Mohs Hardness	–	7	6	8
Electric resistance	Ω cm	10^{14}	10^{6}	10^{5}
Melting point	°C	1610	1825	2015
Heat conductivity (300 K)	W m^{-1} K^{-1}	1.38	8.4	36

2.1.1 Purity

AEROSIL® fumed silica has a SiO_2 content of more than 99.8% and is pure amorphous silica. Its very low water content and the absence of any salts are an important feature guaranteeing excellent performance as an external additive. Very high purity levels also characterize AEROXIDE® fumed alumina and AEROXIDE® fumed titanium dioxide.

2.1.2 Surface Area and Structure

The BET Specific Surface Area values of our AEROSIL® and AEROXIDE® grades range from 50 to 380 m^2/g. This parameter alone reveals much about the particle structure of the grade and hence much about its physical-chemical properties and performance. For instance, it is well known that fumed silica and fumed metal oxide particles owe their unique performance to the fact that while in their native state they are quite large, roughly between 10 µm and 100 µm, but under shear forces these particles divide into smaller fractal units (generally larger than 0.1 µm) that can completely cover the toner surface.
The mastery of this relationship between large, native powder particles (we call “agglomerates”) and dispersed, fractal units (we call “aggregates”) is key (**Figure 4**).
Converting the native agglomerates to well dispersed aggregates unlocks the value of these fascinating materials in diverse applications, not the least including toner formulations.

For the toner formulator what the BET Specific Surface Area also indicates is the degree of this coverage: large BET Surface Areas mean greater coverage while smaller BET grades mean that the aggregates sit more prominently on the toner surface and therefore cover it less completely. On an even finer level, we recognized that control of the degree of internal structure is also possible.

This is particularly demonstrated with the low surface area materials (BET = 50 m²/g). Therefore we offer two distinct lines of products with this BET characteristic: Low Structure/Low BET (such as AEROSIL® RY 50 and AEROSIL® RX 50, both with average BET = 50 m²/g) versus High Structure/Low BET (such as AEROSIL® NY 50 and AEROSIL® NAX 50, also both with average BET = 50 m²/g).

Specific Surface Area (BET) plays a central role in understanding the performance of a particular grade for example, while products with medium to high specific surface area (150 m²/g and higher) are excellent free-flow and strong tribo-charging agents, external additives with lower surface area (below 150 m²/g) are effective spacers between toner particles and thereby improve durability – i. e. charge stability under long run conditions. We have also seen that grades with low structure/low surface area minimize Organic Photo-Conductor (OPC) roll build-up and that high surface area materials are critical to maintaining charge stability – and so it goes! Therefore, organizing around BET surface area is a useful design that we feel provides the toner formulator with the most accurate and predictive power. It is the basis of our approach to provide the most complete service to the toner manufacturing industry.

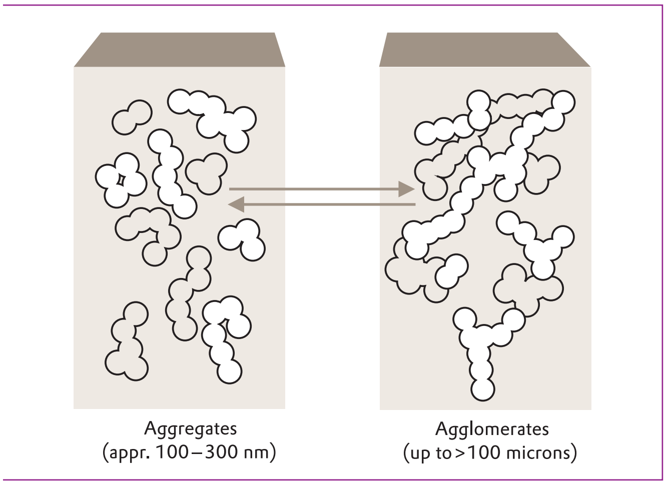


Figure 4
Schematic representation of AEROSIL® fumed silica and/or AEROXIDE® fumed metal oxide aggregates and agglomerates. Primary particles do not exist as such but form larger aggregates and agglomerates well above 100 nm in size even though the toner industry usually describes external additives by their primary particle size.

2.2 Surface Treatment

The core particles of untreated AEROSIL® fumed silica, AEROXIDE® fumed alumina, and AEROXIDE® fumed titanium dioxide carry M-OH hydroxyl groups (M = Si, Al, Ti) on their surfaces. As a result, they have a high affinity for water (i. e. they are hydrophilic).

When organo-silicon compounds, silicone oils and/or organic groups are reacted with the surface hydroxyl groups, they are chemically bound to the metal oxide surface. The resulting products are then no longer wetted by water – they are hydrophobic – and when dispersed on a toner surface impart resistance to moisture pick-up by the toner. The surface treatment also makes fumed metal oxides easier to disperse and substantially increases their free-flow enhancing and tribo-charging properties. For toner applications, most efficient are dimethyl-silyl-, trimethylsilyl-, and polysiloxane groups, all of which make the tribo-charge more negative. As discussed before, the tribo-charge is not only determined by the surface treatment but also by the chemical nature of the base metal oxide and its specific surface area.

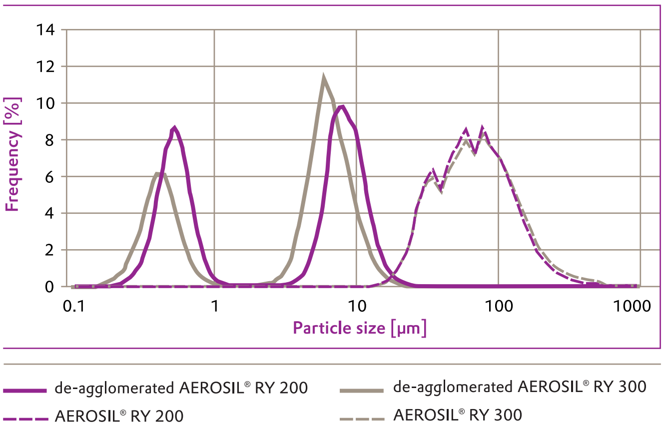
Treatment of fumed silica with silanes carrying amino functional groups (in combination with a hydrophobizing agent) results in AEROSIL® products with a positive tribo-charge. Examples are AEROSIL® NA 50 H, AEROSIL® R 504, and AEROSIL® RA 200 HS.

2.3 De-agglomeration and Structure Modification

To further modify and improve the performance attributes of AEROSIL® and AEROXIDE® products, Evonik developed two mechanical processes: de-agglomeration and structure modification. De-agglomeration deconstructs the fumed oxide agglomerates while the aggregates remain essentially unchanged. Structure modification, on the other hand, refers to the breaking down of aggregates themselves. A very important distinction between the two processes is that de-agglomeration results in a lower bulk density while structure modification raises the powder bulk density. Nevertheless, both processes can substantially improve the dispersibility of fumed metal oxides albeit by different approaches.

Relative dispersibility of an external additive can be described by particle size analysis. In this technique an AEROSIL® sample is dispersed in ethanol, sonicated and analyzed via a laser scattering analyzer. In this way the agglomerates that make up the fumed silica/fumed metal oxide structure are broken down to levels that reflect the relative ease of dispersibility when toner and external additive are mixed together in a dry-blending process. **Figure 5** shows that two unmodified powders (AEROSIL® RY 200 and AEROSIL® RY 300), when dispersed in ethanol and analyzed, show average particle sizes of approximately 100 micrometers.

Figure 5 Particle size distribution of regular AEROSIL® fumed silica grades and the corresponding de-agglomerated products (dispersion in ethanol, 1 minute sonication, Horiba LA 920).



On the other hand, the corresponding de-agglomerated products disperse much easier and result in considerably smaller particle sizes. While exactly comparing this wet-dispersion method with the true dry-mixing process of toner production is an exaggeration, it is clear that the de-agglomeration process significantly modifies the AEROSIL® external additive and improves its dispersibility. The difference between an untreated and a structure-modified AEROSIL® product can be seen in the transmission electron microscopic images in **Figure 6**.

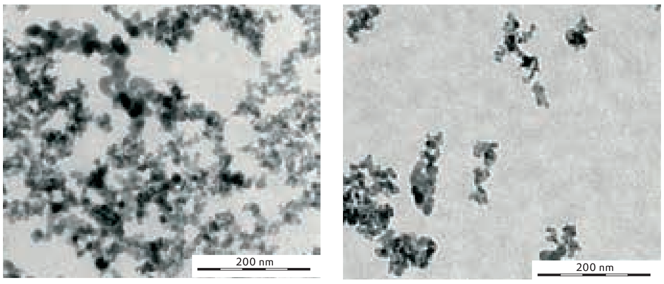


Figure 6
Transmission electron microscopic images of regular AEROSIL® fumed silica (left) and the corresponding structure-modified AEROSIL® R 8200 (right)

While both products show similar BET Surface Area, the structure-modified product (**right picture**) consists of considerably smaller aggregates than regular structured AEROSIL® products. Structure-modified products, examples are AEROSIL® R 8200 and AEROSIL® R 9200, are consequently easy to disperse and do not re-agglomerate. In addition, they are characterized by substantially higher bulk and tapped densities facilitating handling and storage.

3 Toner Formulation with AEROSIL® and AEROXIDE® External Additives

3.1 General Guidelines

AEROSIL® fumed silica has been used as external additive in toner since the 1970ies. At the beginning, AEROSIL® R 972 (dimethyldichlorosilane treated fumed silica) was the most widely used additive. This material has a moderate degree of hydrophobicity and imparts good free flow to toners at low addition rates such as 0.1–0.3 %. With such additives, the toner charge is controlled mainly by addition of charge controlling agents (CCA).

In recent years, external additive requirements for toners going into printer and copying machines have diversified due to a variety of system developments such as multi-purpose use, the trend to smaller machines, energy-saving, and new application areas like digital presses for high volume and on-demand printing. Due to this increase in system complexity, more accurate material design is needed in the development of very fine particle toners, chemically produced toners, and color toners. As a result, modern toners use combinations of several external additives for a total concentration of up to 5 %.

To optimize selection of an external additive for toner, several factors need to be considered: type of toner (monochrome or color; milled or chemically produced), the type of machine (analog or digital), and the type of photo-conductor (PC) drum (amorphous-silicon: a-Si or Organic Photo-Conductor: OPC). The complex role played by external additives used for toners is depicted in **Table 2**.

Table 2 Required properties in design with external additives at each stage of the printing process

Process Step	Additive Design Factor
Storage	Environmental Stability Anti-caking Charge Stability
Feed	Flowability Admixing
Mixing	Electrification Speed Dispersibility Admixing
Development	Electrification Separation from Carrier Admixing Environmental Stability
Transfer/Separation	Electrification Adhesiveness De-agglomeration
Cleaning	Particle Size De-agglomeration Flowability Adhesiveness

An appropriate external additive is selected by considering its physical-chemical properties (surface area, type of metal oxide and surface treatment) and then confirming the selection through complete applications tests. With the advancing requirements of electro-photography such as better image quality and higher process speeds, the need for more diverse as well as more durable external additives has made their selection process by the formulator more complex and critical (**Table 3**).

3.2 Selecting the Right External Additive

The tables on the following pages rank specific AEROSIL® fumed silica and AEROXIDE® fumed metal oxide based external additive grades with regard to various critical performance attributes. Of course these rankings are also dependent on the toner used and the manufacturing process; however general formulating principals can be understood from considering the trends and relationships illustrated within the tables.

3.2.1 Toner Flow

Two theories have been developed to describe the mode of action of fumed silica as a free-flow agent;[3] either explains the improvement of toner flow obtainable with external additives.

The fine particles of AEROSIL® fumed silica and/or AEROXIDE® fumed metal oxides, predominately aggregates and small agglomerates, adhere to the surface of toner particles. The aggregates then act as spacers and by increasing the distance between the toner particles result, in a reduction of the attractive forces between them (**Figure 7**).

Table 3 Trends in electro-photography and their impact on the use of external additives

Commercial and technical trends	Impact from fumed inorganic materials
Monochrome towards color toner	• Titanium dioxide & silicon/titanium mixed oxides as low resistivity material
Milled toner towards chemically produced toner	• Higher diversity in additives due to larger variety in toner particle morphology • De-agglomerated additives for more "gentle" incorporation • Low BET Surface Area silica and/or titania as spacer to improve durability
Organic PC versus amorphous silicon PC	• More abrasive external additives like alumina facilitate drum cleaning
Electro-photographic color printing presses	• Tailored external additive combinations • Low BET Surface Area silica and/or titania as spacer to improve durability • Titanium dioxide & silicon/titanium mixed oxides as low resistivity material
Low cost color printers	• Sometimes combination of lower cost external additives – even hydrophilic silica
Toner resins with lower fusing temperatures (T_g)	• More abrasive external additives like alumina facilitate drum cleaning
Smaller toner particles	• Tailored external additive combinations • De-agglomerated additives for more "gentle" incorporation.

Additionally, at higher humidity levels, external additives disrupt the film of adsorbed water on the toner surface which also lowers the attractive forces between them.

The second theory can be described as a ball bearing type of action. The particles of an external additive form a mono-particulate layer on the toner particles reducing the frictional and adhesive forces that operate between the surfaces.

Figure 7 Particles stick together by van der Waals and other forces of attraction (left). The higher the product's BET Surface Area, the more pronounced the effect. AEROSIL® fumed silica and/or AEROXIDE® fumed metal oxide aggregates act as a spacer between the particles. Attraction forces decrease with increasing distance between particles (right).

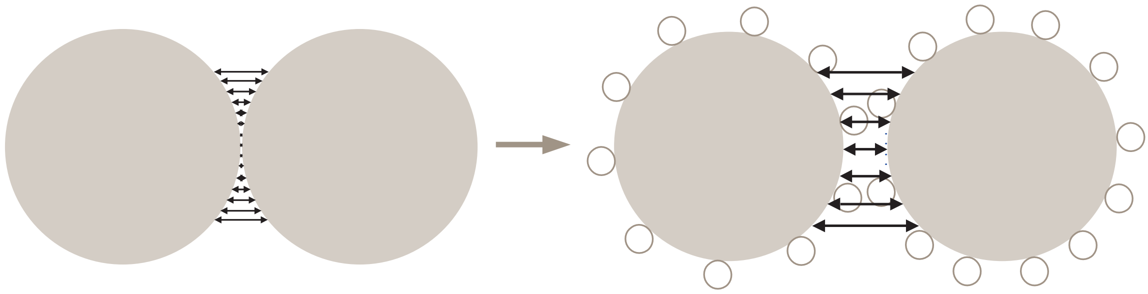
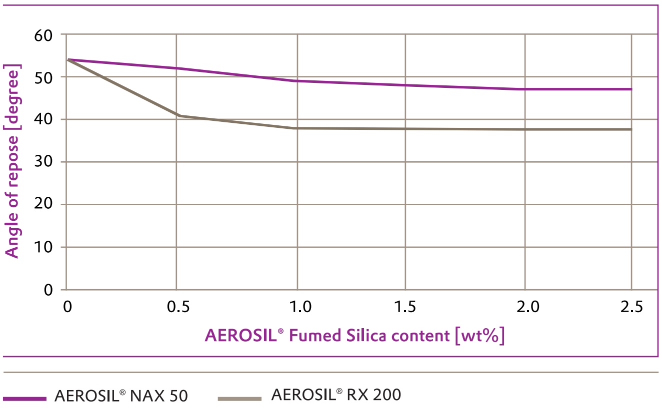


Figure 8 Effect of AEROSIL® external additive content on toner flow of a toner formulation containing low and high BET fumed silica, respectively. Improved toner flow results in a lower angle of repose (compare to chapter 5).



As a general rule, the larger the BET Surface Area of an external additive, the higher the flowability the additive imparts to the toner formulation. At comparable usage levels therefore AEROSIL® 200 and AEROSIL® 300 external additives provide higher toner free-flow than do grades with lower BET Surface Area. Surface modification will also affect toner flow. Generally AEROSIL® fumed silica additives treated with Hexamethyldisilazane (HMDS) result in toner with the highest flowability, followed by those treated with Dimethyldichlorosilane (DDS).

Dimethylpolysiloxane (PDMS) treated fumed silica additives are generally more difficult to disperse compared with DDS and HMDS treated products, thus their effect on flowability is lower than the others. An efficient free-flow agent, however, is the de-agglomerated AEROSIL® RY 200 L (**Table 4**).

3.2.2 Tribo-charge

The tribo-charge of a toner particle can be controlled to a large extent by the right choice of external additive(s). Surface state models of tribo-charging have been successful in explaining many features of the charging of electrophotographic toner.[4]

Due to its high purity and very low water content, AEROSIL® fumed silica is an excellent insulator or, in other words, has a very high electrical resistance. It is therefore capable of building up and carrying high electrostatic charges when colliding with other particles. The term “tribo-charging” is usually used in toner technology as it refers to the generation of electrostatic charge through friction between surfaces. This property makes AEROSIL® fumed silica very efficient in controlling and adjusting the charge characteristics of a toner in a well-defined manner. In essence, the toner surface takes on the characteristics of a fumed silica surface and charges more negatively.

Table 4 AEROSIL® and AEROXIDE® External Additives – **Effects on Toner Flow**

	AEROSIL®							AEROXIDE®				
	SiO_2							SiO_2/TiO_2		TiO_2	TiO_2	Al_2O_3
BET Surface Area m²/g	50	50	90	130	150	200	300	45	80	50	90	100
DDS				R 972		R 974 R 9200	R 976 R 976 S					
PDMS	RY 50	NY 50		RY 200 S	R 202	RY 200 RY 200 L	RY 300					
HMDS	RX 50	NAX 50	NX 90 G NX 90 S	NX 130		RX 200 R 8200	R 812 R 812 S RX 300	STX 501	STX 801			
HH + AS		NA 50 H NA 50 Y	REA 90	VP NA 130 Y		R 504 REA 200 RA 200 HS NA 200 Y						
RS						R 805				T 805	NKT 90	C 805
D4						R 104	R 106					

R 812 S	High
RX 200	
R 972	
RX 50	
RY 50	Low

DDS = Dimethyldichlorosilane, PDMS = Polydimethylsiloxane, HMDS = Hexamethyldisilazane, HH = HMDS or PDMS, AS = Aminosilane, RS = Alkylsilane, D4 = Tetra (dimethylsiloxane). Developmental products are labeled with the VP designation.

The level of tribo-charge is a function of both the specific surface area and the chemical nature of the AEROSIL® fumed silica grade. Treatment of a toner with fumed silica increases its work function in proportion to the fractional toner surface coverage with fumed silica. This means that fumed silica with a high specific surface area is more efficient than one with a low specific surface area at comparable usage levels. Additionally, toner treated with hydrophobic fumed silica charges more negatively than toner treated with hydrophilic silica.[4,5,6]
The most negative tribo-charge is thus provided by hydrophobic AEROSIL® grades with a high specific surface area such as AEROSIL® RY 300, AEROSIL® RX 300 and AEROSIL® R 812 S.

Creating positively charged toner particles or balancing an excessive negative tribo-charge requires an external additive with a positive tribo-charge such as amino-silane treated in combination with a hydrophobizing agent -grades such as AEROSIL® NA 50 H, AEROSIL® R 504, and AEROSIL® RA 200 HS.

Both titanium dioxide and alumina have a considerably lower electrical resistance than fumed silica and therefore a less negative tribo-charge. Untreated fumed alumina, such as AEROXIDE® Alu C has an even slightly positive tribo-charge when agitated with a ferrite carrier whereas surface treated AEROXIDE® Alu C 805 charges slightly negative. Particularly effective titanium dioxide products are AEROXIDE® TiO_2 NKT 90 and our novel fumed Silicon/Titanium mixed oxide AEROXIDE® STX 801 and AEROXIDE® STX 501 (for more information on the latter product please refer to **Chapter 3.3.2**). A more cost-efficient alternative is AEROXIDE® TiO_2 T 805. All metal oxides described here provide stabilized charge-up behavior under long activation times in both L/L and H/H conditions. The q/m of toner surface treated with these fumed metal oxides is low and nearly independent of humidity.

Generally, it is not easy to predict the tribo-charge of a toner formulation only by the selection of the external additive(s) because it is highly dependent on the complete toner formulation and printer design (**Table 5**).

Table 5 AEROSIL® and AEROXIDE® External Additives – **Effects on Toner Tribo-Charge**

	AEROSIL®							AEROXIDE®				
	SiO_2							SiO_2/TiO_2		TiO_2	TiO_2	Al_2O_3
BET Surface Area m^2/g	50	50	90	130	150	200	300	45	80	50	90	100
DDS				R 972		R 974 R 9200	R 976 R 976 S					
PDMS	RY 50	NY 50		RY 200 S	R 202	RY 200 RY 200 L	RY 300					
HMDS	RX 50	NAX 50	NX 90 G NX 90 S	NX 130		RX 200 R 8200	R 812 R 812 S RX 300	STX 501	STX 801			
HH + AS		NA 50 H NA 50 Y	REA 90	VP NA 130 Y		R 504 REA 200 RA 200 HS NA 200 Y						
RS						R 805				T 805	NKT 90	C 805
D4						R 104	R 106					

R 504	Positive
NKT 90	Weakly Negative
RY 50	
R 972	
RX 300	Strongly negative

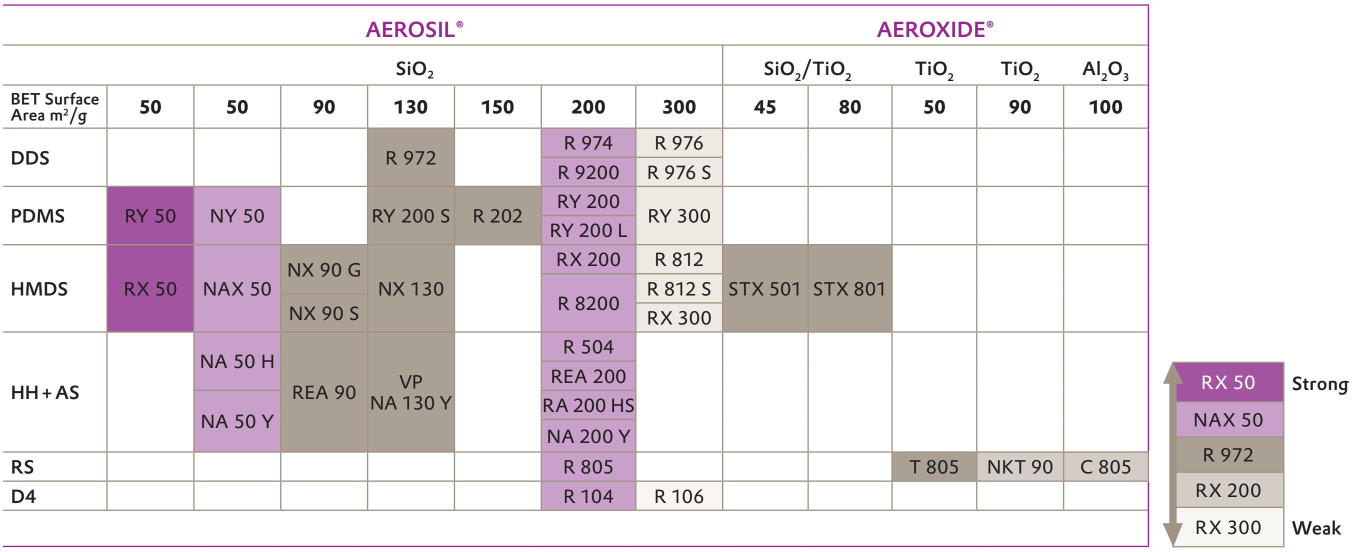
DDS = Dimethyldichlorosilane, PDMS = Polydimethylsiloxane, HMDS = Hexamethyldisilazane, HH = HMDS or PDMS, AS = Aminosilane, RS = Alkylsilane, D4 = Tetra (dimethylsiloxane). Developmental products are labeled with the VP designation.

3.2.3 Spacer

Toner resins with low glass transition temperatures (T_g) in combination with long agitation times, as they occur in office printers and commercial printing presses, raise the likelihood that external additives become embedded into the toner particles and thereby lower their performance, sometimes to the complete breakdown of the printing process. To counteract this, external additives with relatively low surface area such as AEROSIL® RY 50 and AEROSIL® RX 50 should be considered when designing the external additive composition.

These additives act as spacers between colliding toner particles and keep small primary particle size additives, for example AEROSIL® RX 300 or AEROSIL® R 812 S well dispersed on the toner surface for optimal free flow and tribo-charging. Such additives also maintain a separation between the toner particle and the optical photo-conductor (OPC) drum, reducing toner build-up.

Table 6 AEROSIL®and AEROXIDE® External Additives – **Spacer Effect**



	AEROSIL®							AEROXIDE®				
	SiO_2							SiO_2/TiO_2		TiO_2	TiO_2	Al_2O_3
BET Surface Area m^2/g	50	50	90	130	150	200	300	45	80	50	90	100
DDS				R 972		R 974 R 9200	R 976 R 976 S					
PDMS	RY 50	NY 50		RY 200 S	R 202	RY 200 RY 200 L	RY 300					
HMDS	RX 50	NAX 50	NX 90 G NX 90 S	NX 130		RX 200 R 8200	R 812 R 812 S RX 300	STX 501	STX 801			
HH + AS		NA 50 H NA 50 Y	REA 90	VP NA 130 Y		R 504 REA 200 RA 200 HS NA 200 Y						
RS						R 805				T 805	NKT 90	C 805
D4						R 104	R 106					

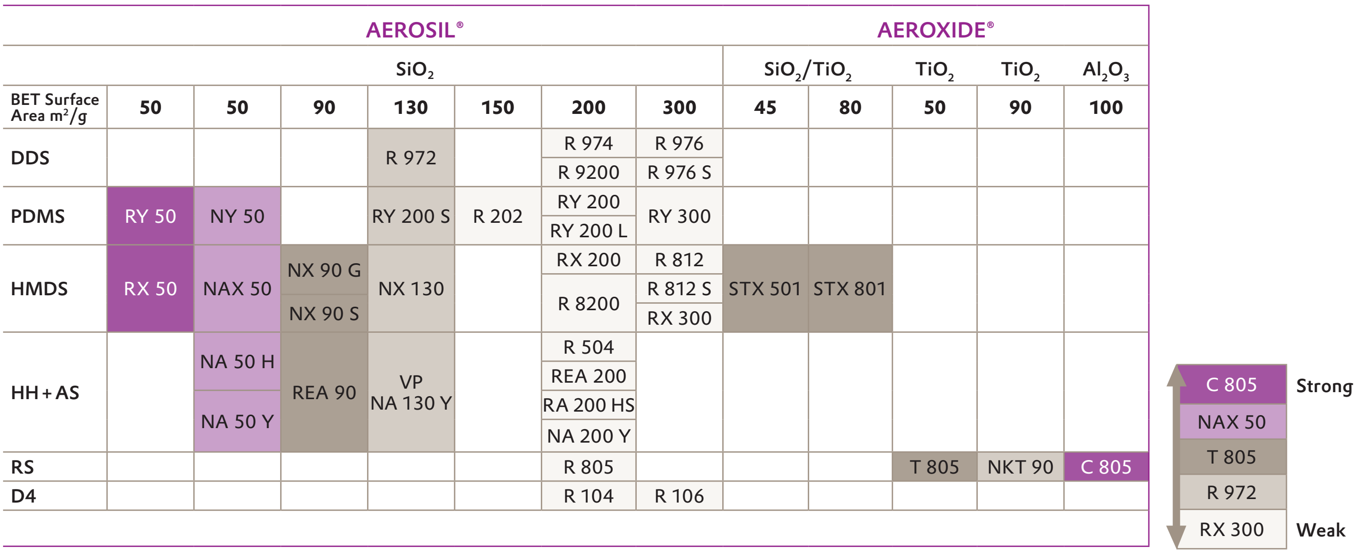
RX 50	Strong
NAX 50	
R 972	
RX 200	
RX 300	Weak

DDS = Dimethyldichlorosilane, PDMS = Polydimethylsiloxane, HMDS = Hexamethyldisilazane, HH = HMDS or PDMS, AS = Aminosilane, RS = Alkylsilane, D4 = Tetra (dimethylsiloxane). Developmental products are labeled with the VP designation.

3.2.4 OPC Drum Polishing/Cleaning Aid

Toner build-up ("filming") on the OPC surface can be addressed by using external additives which either have a high Mohs hardness or consist of medium to large primary particles. In this way, additives such as AEROSIL® RX 50 and AEROSIL® RY 50 not only reduce embedding, as described in the previous chapter, but also function as a polishing and/or cleaning aid. As an alternative strategy, AEROXIDE® Alu C 805, because of its relatively high Mohs hardness (compare to **Table 1**), displays distinct value as a polishing aid even though its primary particle size is relatively moderate.[7] The polishing/cleaning effect of Evonik external additives is shown in **Table 7**.

Table 7 AEROSIL® and AEROXIDE®External Additives – **Polishing/Cleaning**



	AEROSIL®							AEROXIDE®				
	SiO_2							SiO_2/TiO_2		TiO_2	TiO_2	Al_2O_3
BET Surface Area m^2/g	50	50	90	130	150	200	300	45	80	50	90	100
DDS				R 972		R 974 R 9200	R 976 R 976 S					
PDMS	RY 50	NY 50		RY 200 S	R 202	RY 200 RY 200 L	RY 300					
HMDS	RX 50	NAX 50	NX 90 G NX 90 S	NX 130		RX 200 R 8200	R 812 R 812 S RX 300	STX 501	STX 801			
HH + AS		NA 50 H NA 50 Y	REA 90	VP NA 130 Y		R 504 REA 200 RA 200 HS NA 200 Y						
RS						R 805				T 805	NKT 90	C 805
D4						R 104	R 106					

C 805	Strong
NAX 50	
T 805	
R 972	
RX 300	Weak

DDS = Dimethyldichlorosilane, PDMS = Polydimethylsiloxane, HMDS = Hexamethyldisilazane, HH = HMDS or PDMS, AS = Aminosilane, RS = Alkylsilane, D4 = Tetra (dimethylsiloxane). Developmental products are labeled with the VP designation.

It is clearly seen in **Figure 9** that AEROSIL® RY 50 and AEROSIL® NY 50, fumed silica types with a medium to low BET Surface Area, as well as AEROXIDE® Alu C 805, a surface-treated size fumed alumina, result in fast reduction of film thickness on a model OPC drum while large BET Surface Area fumed silica additives have almost no impact.[7]

Figure 9 Effect of external additives as polishing aid on the toner film (residue) thickness on an OPC model surface as a function of time.

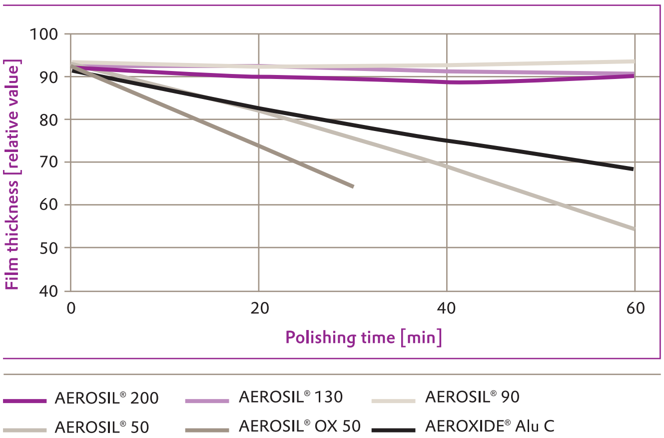
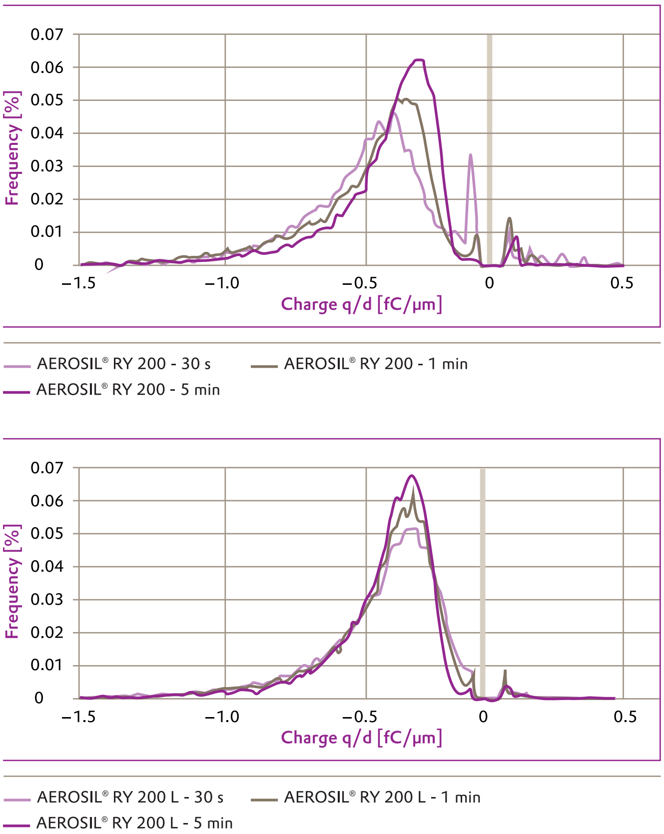


Figure 10 Frictional electrification time of a toner after blending with AEROSIL® RY 200, a regular fumed silica additive (**upper picture**) in comparison to AEROSIL® RY 200 L, a de-agglomerated fumed silica additive (**lower picture**).



3.3 Novel External Additives

3.3.1 De-agglomerated External Additives

As is emphasized throughout this brochure the complete conversion of agglomerates to aggregates (the dispersed particles on the toner surface with sizes greater than 0.1 µm) is essential to optimal performance. The conversion requires shear energy (either in the form of increased mixing speed or time) – and certain grades because they are made up of high surface area silicas or particularly cohesive surface modifications require even increased energy. If the toner formulator could start with a de-agglomerated grade some of this need for energy addition might be avoided. Evonik has considered this need and developed what we call de-agglomerated grades precisely for this purpose. In general, de-agglomerated additives can be dispersed with considerably less shear energy on the toner surface. The resulting distribution of aggregated particles on the toner surface is then more homogeneous and allows for faster "charge-up", a critical requirement for all new generation printers. As illustrated in **Figure 10**, the rate of convergence, in other words, the charge-up of toner with de-agglomerated fumed silica is much faster compared to a toner with regular fumed silica. De-agglomerated AEROSIL® fumed silica grades are especially efficient for toner made from low T_g resins which require gentle mixing with lower shear forces in order to not affect the toner morphology.

3.3.2 Fumed Silicon-Titanium Mixed Oxides

Titanium dioxide is used in color toners to control charge stability and charge distribution but it has the disadvantage that even with organic surface treatment the particle does not exhibit strong hydrophobicity. This is in contrast to a similarly treated fumed silica particle. The reason for this difference is believed to originate in the relatively higher concentration of hydroxyl-groups on the titanium dioxide surface in comparison to silica. Adding a silica shell onto a titanium dioxide core has been found to overcome this disadvantage and as a result fumed silicon/titanium mixed oxides can provide a satisfactory charge distribution, excellent speed in electrification and even a better charge stability than pure titania (**Table 8**). The properties of silicon/titanium mixed oxides can be further tailored by modification of the silica content and other structural parameters to match the requirements of each basic formulation.[8,9]

We particularly recommend AEROXIDE® STX 801 and AEROXIDE® STX 501, both hydrophobized fumed silicon-titanium mixed oxides with a titanium dioxide core and a silica shell (see **Figure 3**). These products combine the tribo-charging attributes of titanium dioxide with the surface properties of silica. Its high hydrophobicity is imparted by trimethylsilyl-groups which are firmly anchored to the silica surface.

Table 8 Comparison of the electrification behavior of fumed silica, AEROXIDE® STX 801 and fumed titania

	Fumed silica	AEROXIDE® STX 801	Fumed titania
Tribo-charge	High	Medium	Low
Charge Distribution	Wide	Middle	Narrow
Charge-up Speed	Quick	Quick	Slow
Charge Stability	Low	High	Medium

4 Manufacturing with AEROSIL® and AEROXIDE® External Additives

When using AEROSIL® and AEROXIDE® external additives various parameters affect the performance characteristics of the final toner formulation. These parameters can be roughly classified as follows:

1. Powder characteristics of the external additive (particle type, particle size, surface treatment etc.)
2. Compatibility of the external additives with the toner formulation
3. Blending of the toner with the external additive

Characteristics of the external additives are determined by the aforementioned properties, such as core particle composition, particle size and surface treatment. Therefore, it is necessary to select external additives according to the desired function(s) of the toner.

Printing performance of the toner is greatly affected by the toner formulation, so external additive/toner matrix compatibility is crucial. Even if a certain type of fumed silica shows satisfactory performance with one specific toner matrix, this does not mean that it can be applied to every other toner formulation.

Blending of toner with the external additive also has a tremendous impact on final toner performance. As described above, the breakdown of the AEROSIL® fumed silica and AEROXIDE® fumed metal oxide agglomerates is fundamental to optimal performance – this breakdown of agglomerates to dispersed aggregates is accomplished during toner processing and as such, critical parameters to performance include: the type of toner, mixing time & temperature, and mixer type. Severe mixing conditions should be avoided since they may damage the toner particles resulting in diminished performance.

An external additive may also be milled prior to blending with the toner. This breaks down larger agglomerates and saves mixing energy and time. A very convenient and cost-efficient method to avoid a pre-milling step is the use of Evonik´s de-agglomerated AEROSIL® grades, described in Chapter 3.3.1.

Very often, not just one but combinations of two or more external additives are used. Methods of mixing two types of external additives – fumed silica having a low BET Surface Area (e.g. AEROSIL® RY 50 or AEROSIL® RX 50) and fumed silica having a high BET Surface Area (e.g. AEROSIL® R 812 S or AEROSIL® RY 300) – are summarized in **Figure 11**.

Figure 11 Mixing high BET and low BET fumed silica combinations as external additives

Effect
High BET silica → flow
Low BET silica → durability

Admix Low and High BET silica at one time (Simple Process)

High BET silica is added first to give high flowability (Easy to Disperse)

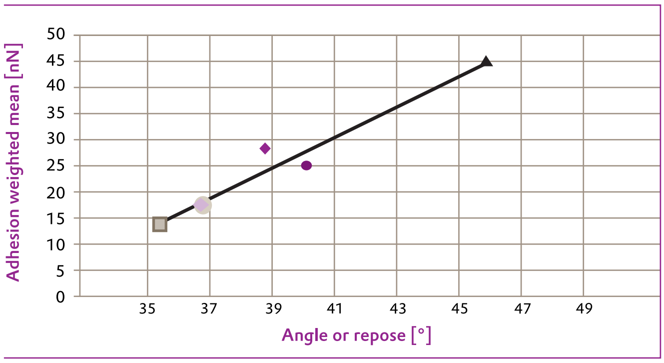
Low BET silica is added first to give high durability (Prevents Embedding)

Admix Low BET and High BET silica before adding to the toner
(High BET silica gives flowability and dispersibility to Low BET silica)

5 Agglomeration and Mixing Studies

In extensive studies carried out in cooperation with the University of Tuebingen,[10] Evonik investigated the influence of type of substrate, type of mixer, and mixing conditions on the size of AEROSIL® fumed silica agglomerates and aggregates, and as a result the flow behavior of the substrate. Scanning Electron Microscopy (SEM) and X-Ray Photoelectron Spectroscopy (XPS) analyses of mixtures of microcrystalline cellulose powder, one of the model substrates used in the study, and AEROSIL® fumed silica showed a clear correlation between the degree and uniformity of coverage with fumed silica particles on the powder's surface and the flow enhancement exerted by the fumed silica. While the soft agglomerates of hydrophobic AEROSIL® R 972 V reached their final size and optimal distribution under gentle mixing conditions, higher mixing energies were required to break up the agglomerates of hydrophilic AEROSIL® 200 products to achieve uniform coverage. It was additionally found, that the "microscopic" attractive forces between particles determined by Atomic Force Microscopy directly correlate with the macroscopic flowability (angle of repose) (**Figure 12**).[11]

Figure 12 Correlation of atomic force microscopy data to the angle of repose measurements on mixtures of microcrystalline cellulose and various AEROSIL® grades.[3]



This study demonstrated that mixing conditions need careful attention to ensure optimal dispersion of free-flow agent particles on the powder's surface. Severe mixing conditions should be avoided since they may damage the powder and reduce its particle size, resulting in decreased flowability.

Additionally, it was found that moisture uptake of powders is not influenced by any of the fumed silica types used; rather water adsorption is characteristic of the powder itself. However, even after equilibrating at high humidity levels, all powder mixtures containing AEROSIL® fumed silica maintained good flowability, while the flowability of the pure powders turned strongly cohesive. Hydrophobic grades were especially efficient in this case.

6 Product Safety

AEROSIL® fumed silica and AEROXIDE® fumed metal oxides are used in a wide range of applications. Therefore the toxicological profile of these materials is of great importance with respect to both consumer and workers safety.

Fumed silica, alumina, and titanium dioxide are regarded as safe with regard to acute toxicity, skin irritation, skin sensitization, mutagenity and reproductive toxicity. Also, repeated dose exposure to skin and oral intake did not give any critical result.

6.1 Fumed Silica

Synthetic silica products such as AEROSIL® fumed silica are completely amorphous and do not contain any crystalline domains. This was determined by transmission electron microscopy and X-ray diffraction. These methods are very precise with detection limits less than 0.01% by weight.

In numerous inhalation studies with synthetic amorphous silica, none of the products tested caused irreversible lung damage or progressive damage comparable to silicosis ("dust lung"), which are possible health risks resulting from exposure to crystalline dusts. Epidemiological studies on workers with long-term exposure to fumed silica have also not shown any evidence of silicosis. Similarly, the available data do not provide any indication of other permanent respiratory disease resulting from fumed silica.[12]

6.2 Fumed Titanium Dioxide

In 2006 the International Agency for Research on Cancer (IARC) reclassified titanium dioxide (titania) as a class 2B substance (possibly carcinogenic to humans). The reclassification of titania regarding the risk of lung cancer is based on studies on the impact of inorganic fine particulates in animals.

As for the long term exposure to fumed titanium dioxide, regular medical check-ups were carried out at Evonik titanium dioxide manufacturing facility in Germany (Rheinfelden) over a number of years. No evidence of a higher incidence of respiratory diseases compared with the general population was found. These findings were confirmed by subsequent epidemiological studies by other European and US titanium dioxide producers. These producers, together with Evonik Industries, examined the impact of inhaled titanium dioxide dust in studies where rats, mice, and hamsters were exposed to air containing different concentrations of titanium dioxide dust for up to 90 days. Importantly, all three species exhibited changes to lung tissue only after exposures to extremely high doses (250 mg/m^3). At a lower concentration of 0.5 mg/m^3, which corresponds to the level found at Evonik manufacturing facility, no tissue damage was found. At 2 mg/m^3, which is the workplace exposure limit in Germany, slight changes in tissue were observed only in rats.

Evonik also investigated whether titania aggregates and agglomerates, as found in titania dust in workplaces, can disintegrate in lung tissue to form particles smaller than 0.1 µm. Model calculations were used to determine whether the main surfactant found in lung tissues – dipalmitoyl phosphatidylcholine (DPPC) – is capable of splitting the bonds within titania particles. This could only occur if the bond energy between the titania surface and DPPC is higher than between TiO_2 particles. The model calculation showed that 1 J/m² is needed to split the hydrogen bonds within titania agglomerates. Breaking up the stronger Ti-O-Ti bonds within titania aggregates would require 10 J/m². However, the bond energy between the titania surface and DPPC was calculated as only 0.05 J/m² and is thus far weaker.

The calculated results were then validated in laboratory trials simulating physiological conditions: Various concentrations of DPPC were added to buffered titania dispersion with a pH of 6.5 and the particle size distribution was determined. It was found that the addition of DDPC had no impact on the particle size distribution and no isolated particles below 100 nm could be detected. These results indicate that disintegration of titania aggregates and agglomerates into primary particles under physiological conditions is very unlikely.

Additional information on can be found in the leaflet "Health Protection in the Production and Processing of Titania" which is available in English, German and Japanese.

7 Storage and Handling

Depending on the grades, AEROSIL® fumed silica and AEROXIDE® fumed metal oxide products are packaged in 5 kg, 10 kg (22 lbs), 15 kg, and 20 kg paper bags, respectively. Carton boxes or shrink-wrapped pallets are usually used for shipment.

AEROSIL® fumed silica and AEROXIDE® fumed metal oxides are chemically very stable and can be stored unchanged for many years. Because of their high specific surface area, however, they can adsorb volatile substances from the environment. In particular, the adsorption of water can greatly influence their performance. Additionally, agglomeration and aggregation can occur under pressure and diminish dispersibility when bags/pallets are stacked too high or stored under a heavy load for an extended period of time.

We therefore recommend to store AEROSIL® fumed silica and AEROXIDE® fumed metal oxides in closed containers in a dry place protected from volatile substances and using within two years after the date of manufacture. Some more delicate products should be used within one year after the day of manufacture. The best way of protecting workers and the environment when processing AEROSIL® and AEROXIDE® products is to use closed production systems that prevent particle emissions as much as possible. Additional technical precautions such as filters, extraction system and personal protective equipment are used where necessary to optimize environmental protection and occupational health and safety. Regular measurement of particulate concentrations in the workplace and medical check-ups make sure these measures are effective.

8 Experimental Section

8.1 Determination of Tribo-Charge

50 g of a non-coated ferrite carrier and 0.1 g of the AEROSIL® fumed silica or AEROXIDE® fumed metal oxide under investigation were put into a 75-ml glass container, covered with a cap, and shaken for five minutes using a TURBULA® mixer. Subsequently, 0.1 g of the mixture was taken out, and subjected to nitrogen blowing for 1 minute by use of a blow-off static electrometer (TB-200 Model from Toshiba Chemical). The measurement was performed at a temperature of 25 °C and a relative humidity of 55 %.

8.2 Preparation of Toner Samples

The toner used in this study was a conventional, milled, negative, styrene-acrylic based toner with an average diameter of 8 µm. 1.0 % of the AEROSIL® fumed silica or AEROXIDE® fumed metal oxide under investigation was added and the resulting mixture was blended for 1 minute at 600 rpm, and subsequently for 3 minutes at 3000 rpm in a high-speed mixer (Super Mixer Piccolo, Kawata Mfg., Co., Ltd.).

8.3 Determination of Toner Flow

The angle of repose of a toner formulation was measured with a Powder Tester PT-S (Hosokawa Micron). 20 g of a toner formulation prepared as describe in the previous paragraph were put on a 355 µm sieve. Sieving was conducted, with vibration through a glass cone onto a round table. The glass cone was mounted above the top of the round table, the distance between the cone and round table was 6.5 cm, and the diameter of the round table was 8 cm. Measurements were conducted in triplicate for each toner sample.

8.4 Determination of Electrostatic Charge Distribution

The electrostatic charge distribution of toner samples were determined by the q-test device (Epping GmbH).

9 Physico-Chemical Data

Property	Unit	**AEROSIL® R 972**	**AEROSIL® R 974**	**AEROSIL® R 9200**	**AEROSIL® R 976**	**AEROSIL® R 976 S**	**AEROSIL® RY 50**
Core material		SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2
BET Surface Area	m^2/g	90–130	150–190	150–190	225–275	215–265	15–45
pH		4.0–5.5	3.8–5.0	3.0–5.0	3.8–5.0	3.8–5.5	4.5–7.5
Drying Loss	%	<0.5	<0.5	<1.5	<1.0	<1.0	<0.5
Carbon content	%	0.6–1.2	0.8–1.4	0.7–1.3	1.0–2.5	1.5–3.0	3.0 – 5.0
Bulk density	g/l	50	50	200	50	50	130
Tribo-charge	µC/g	–410	–450	–190	–600	–680	–110

Property	Unit	**AEROSIL® NY 50**	**AEROSIL® RY 200 S**	**AEROSIL® R 202**	**AEROSIL® RY 200**	**AEROSIL® RY 200 L**	**AEROSIL® RY 300**
Core material		SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2
BET Surface Area	m^2/g	20–40	65–95	80–120	80–120	80–120	110–140
pH		5.0–6.0	4.5–6.5	4.0–6.0	4.0–7.0	4.0–7.0	4.5–5.5
Drying Loss	%	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Carbon content	%	2.5 – 4.0	3.5 – 5.0	3.5–5.0	4.0–6.5	4.0–6.5	6.0–8.5
Bulk density	g/l	60	40	60	50	30	50
Tribo-charge	µC/g	–340	–520	–500	–560	–560	–580

Property	Unit	**AEROSIL® RX 50**	**AEROSIL® NAX 50**	**AEROSIL® NX 90 G**	**AEROSIL® NX 90 S**	**AEROSIL® NX 130**	**AEROSIL® RX 200**
Core material		SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2
BET Surface Area	m^2/g	25–45	30–50	50–80	50–80	80–120	115–165
pH		6.0–8.0	5.5–7.5	5.0–7.5	5.0–7.5	5.5–7.5	5.5–8.5
Drying Loss	%	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Carbon content	%	0.5–1.0	0.5–1.0	0.7–1.5	0.5–1.5	1.0–3.0	1.5–3.5
Bulk density	g/l	170	60	40	40	40	50
Tribo–charge	µC/g	–200	–290	–310	–300	–350	–380

Property	Unit	**AEROSIL® R 8200**	**AEROSIL® RX 300**	**AEROSIL® R 812**	**AEROSIL® R 812 S**	**AEROSIL® NA 50 H**	**AEROSIL® NA 50 Y**
Core material		SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2
BET Surface Area	m^2/g	135–185	190–230	230–290	195–245	30–50	25–45
pH		>5.0	6.0–8.0	5.5–8.0	5.5–7.5	8.0–10.0	6.5–9.0
Drying Loss	%	<0.5	<0.5	<0.5	<0.5	<0.8	<0.8
Carbon content	%	2.0–4.0	2.5–5.0	2.0–3.0	3.0–4.0	0.5–2.0	2.0–4.0
Bulk density	g/l	140	50	60	60	50	40
Tribo-charge	µC/g	–290	–520	–550	–450	+80	+220

All data in this table represent typical values, not specified parameters. Developmental products are labeled with the VP designation. Their commercialization depends on market response.

Property	Unit	AEROSIL® REA 90	VP NA 130 Y	AEROSIL® R 504	AEROSIL® REA 200	AEROSIL® RA 200 HS	AEROSIL® NA 200 Y
Core material		SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2
BET Surface Area	m^2/g	40–70	50–80	125–175	110–150	120–160	100–150
pH		7.5–10.0	6.5–9.5	8.5–11.0	8.0–10.0	8.0–10.0	6.5–9.5
Drying Loss	%	< 1.0	< 1.0	< 1.5	< 1.0	< 0.8	< 0.8
Carbon content	%	3.0–6.0	5.0–7.5	2.0–4.0	5.0–7.5	1.5–3.5	3.5–6.5
Bulk density	g/l	50	30	40	50	40	50
Tribo–charge	µC/g	+ 400	+ 450	+ 350	+ 300	+ 260	+ 260

Property	Unit	AEROSIL® R 805	AEROSIL® R 104	AEROSIL® R 106	AEROXIDE® TiO_2 T 805	AEROXIDE® TiO_2 NKT 90	AEROXIDE® STX 801
Core material		SiO_2	SiO_2	SiO_2	TiO_2	TiO_2	SiO_2/TiO_2
BET Surface Area	m^2/g	125–175	125–175	220–280	35–55	50–75	40–70
pH		3.5–5.5	>4.0	>3.7	3.0–4.0	3.0–4.0	6.0–9.0
Drying Loss	%	< 0.5	< 0.5	< 0.5	< 1.0	< 1.0	< 1.0
Carbon content	%	4.5–6.5	1.0–2.0	1.5–3.0	2.7–3.7	2.5–4.5	0.5–2.0
Bulk density	g/l	60	50	50	200	100	80
Tribo–charge	µC/g	–220	–400	–600	–70	–100	–150

Property	Unit	AEROXIDE® STX 501	AEROXIDE® Alu C 805
Core material		SiO_2/TiO_2	Al_2O_3
BET Surface Area	m^2/g	25–45	85–115
pH		6.0–9.5	3.0–4.0
Drying Loss	%	< 1.0	< 0.5
Carbon content	%	0.2–1.0	3.0–4.5
Bulk density	g/l	140	50
Tribo–charge	µC/g	–100	–130

All data in this table represent typical values, not specified parameters. Developmental products are labeled with the VP designation. Their commercialization depends on market response.

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