## NANO-STRUCTURED PARTICLES TO ENHANCE GREEN COATINGS

Authors: Maria Nargiello*, Dr. Rüdiger Mertsch ${ }^{* *}$, Dr. Günther Michael**, Matt Linares*, Gabrielle Leder**, Dr. Sven Hill** (*Evonik Degussa Corporation, **Evonik Degussa GmbH)

As market and technical focus continues to broaden and expand in the environmentally friendly segments of paints and coatings, so has the portfolio of additive technologies to support and enhance these types of coatings. This paper will deal with particle technology derived from high temperature flame hydrolysis, in the case of $\mathrm{SiO}_{2}$ (Silica) and $\mathrm{Al}_{2} \mathrm{O}_{3}$ (Alumina) and liquid phase reaction in the case of $\mathrm{In}_{2} \mathrm{O}_{3} / \mathrm{SnO}_{2}$ (ITO). The following summarizes the agenda for paper and outlines specific particle technology, coatings attributes enhanced and specific coatings technology, where particle technology is most effective:

Viscosity, Rheological Control, Pigment Suspension \& Coalescence

- Hydrophilic \& Hydrophobic - $\mathrm{SiO}_{2}$ (powder \& dispersed forms)
- High solids, Water, Powder, UV, UV Powder

Anti-Corrosion / Water Repellency

- Hydrophobic $\mathrm{SiO}_{2}$ Technology
- High solids, Water, UV


## Scratch Resistance

- Hydrophobic, SM- $\mathrm{SiO}_{2}$ Technology (powder \& dispersed forms)
- High solids, UV

Free Flow, Fluidization, Transfer Efficiency

- Hydrophilic \& Hydrophobic - $\mathrm{SiO}_{2} \& \mathrm{Al}_{2} \mathrm{O}_{3}$ Technology
- Powder

Transparent IR Absorption and Conductivity

- ITO Technology
- High solids, Water, UV Cured


## Particle Design and Modification

Particle modification technology encompasses three major elements of design to influence performance: core particle identity, surface modification and structure modification (SM). Pyrogenically produced core particles can range in identity, however those notable which are used in coatings include: $\mathrm{SiO}_{2}, \mathrm{Al}_{2} \mathrm{O}_{3}, \mathrm{TiO}_{2}, \mathrm{ZnO} \& \mathrm{CeO}_{2}$.


Flame Hydrolysis of Volatile Metal Compounds $\mathrm{SiCl}_{4} \longrightarrow$ Silicon Dioxide, SA $50-380 \mathrm{~m}^{2} / \mathrm{g}$
$\mathrm{TiX}_{4} \longrightarrow$ Titanium Oxides, SA $50-90 \mathrm{~m}^{2} / \mathrm{g}$
$\mathrm{AlX}_{3} \longrightarrow$ Aluminum Oxides, SA $65-130 \mathrm{~m}^{2} / \mathrm{g}$
$\mathrm{ZrX}_{4} \longrightarrow$ Zirconium Oxide,
Particles resulting from flame hydrolysis are non-porous and typically exist in an aggregated structure of sintered particles. Isolated primary particles do not typically leave the flame. Primary particle size is determined by TEM, and for fumed silica, range from $7-40 \mathrm{~nm}$, with corresponding surface areas of $380-50 \mathrm{~m}^{2} / \mathrm{g}$. For most coatings applications, common primary particle sizes used range from $7-16 \mathrm{~nm}$ with corresponding surface areas from $130-300 \mathrm{~m}^{2} / \mathrm{g}$. Primary particle sizes for Alumina range from $10-20 \mathrm{~nm}$, with corresponding surface areas of
$130-65 \mathrm{~m}^{2} / \mathrm{g}$. The most common surface area used in coatings is $100 \mathrm{~m}^{2} / \mathrm{g}$, though a new higher surface area grade with $130 \mathrm{~m}^{2} / \mathrm{g}$ is being introduced. For hydrophilic grades of fumed metal oxides, surface area, pH and loss on dry (moisture content) are three physical chemical parameters typically measured and reported.

The second element of particle design is surface modification and the main reason for this element is to render hydrophilic particles, hydrophobic in character. Treatment level is measured by C-content (a fourth property typically measured and reported). Different treatments create grades of treated fumed oxides which vary in the level of their hydrophobicity, ratio of the hydrophilic: hydrophobic nature on their surface, tribo-electrostatic charge and thickening efficiency. Typical surface treatments with corresponding attributes are summarized below. Methanol Wettability indicates the consistency of treatment and the balance of hydrophilic: hydrophobic surface.

Table 1.

| Surface Treatment | Impact to Coating |
| :--- | :--- |
| Dimethyl-dichloro-silane (DDS) | "standard" hydrophobization, short surface treatment |
| Trimethoxy-octyl-silane (TMOS) | long chain - hydrophilic / phobic parts (polar systems) |
| Hexamethyl-di-silazane (HMDS) | pH neutral and high hydrophobicity |
| Poly-dimethyl-siloxane (PDMS) | highest hydrophobicity, extractable PDMS amounts |
| Hexa-decyl-silane (HDS, C16) | wets into water |
| Octamethyl-cyclo-tetra-siloxane (D4) | low residual HCl |
| Triethoxy-propyl-amino-silane (TEPAS) + HMDS | highest pH silica - 9, positive electrostatic charge |
| methacryloxypropyl trimethoxy silane (MEMO) | Functional |

Typlcal Muitipoint Methanol Wettability


The third element of particle design is structure modification. The structure of fumed oxides can be modified by one of three proprietary processes. Granulation results in larger, individual spherical particles in the range of 20-30 microns, which are porous and their main function is as free flowing carriers of liquid based actives and oils. Other chemical and mechanical post processes reduce structure (level of aggregation or agglomeration). Fumed silica, structured modified through a proprietary chemical process is used as a reinforcing additive, and retains most of its thickening capabilities (compared to their fully aggregated counterparts). The main feature is due to reduced levels of aggregation at the primary aggregate level, better clarity results. Products resulting from this post processing have significantly higher bulk densities and dramatically reduced thickening efficiency. Such grades are used to enhance scratch resistance and Lotus effect attributes, as higher loading can be achieved with minimal impact to formulation viscosity.

Fumed metal oxides are available as powder and pre-dispersed in water. Selected grades are available in methoxypropylacetate and developments are underway to offer selected grades in monomer for radiation cure coatings.

The remainder of this paper will detail which particle technology is best used to enhance specific coatings attributes in the GREEN coatings segments. Performance attributes of rheology \& coalescence, corrosion resistance, scratch resistance, free flow \& fluidization, and transparent IR \& conductivity are discussed. For more details on particle science, modification and handling please see references 1,2 and 4 .

## Rheology and Coalescence

Fumed silica, in various grades and modifications, has been used for decades in coating formulations to impart thixotropy, anti-settling and anti-sag. The main requirements for best performance are proper selection and adequate dispersion to homogenously distribute aggregates throughout the coating matrix. Proper grade selection can be loosely correlated to polarity, with untreated, hydrophilic fumed silica grades used for non-polar environments and hydrophobically modified grades treated with DDS, TMOS, HMDS found to be more efficient as polarity increases. Specifically for high solids and radiation cure systems, grades treated with TMOS and HMDS are highly effective. Polydimethylsiloxane treated grades, which are the most hydrophobic of all, are often considered in high solids and $100 \%$ solids systems; however care must be taken, as this is the one surface modification which is not fully reacted to the surface and some migratability of free PDMS may cause surface defects and/or adhesion problems. If there is known coatings sensitivity to free PDMS, it is suggested that other surface modified grades be considered.

When optimizing dispersion, to achieve best thickening efficiency and rheological enhancement, several parameters should be taken into consideration. These factors include: shear rate, balancing rate and time, influence of temperature build-up, and sequence of addition. Concerning shear rate: it is suggested that high speed dispersion be used with a saw-type blade and shear rate $>10 \mathrm{~m} / \mathrm{s}$. Under many circumstances, dispersing longer does not compensate for not having adequate shear rate. A typical result of inadequate shear, which results in larger agglomerates still remaining in the coating, is reduced thickening efficiency, deteriorating thix stability over time, lower gloss and surface defects. Concerning the influence of temperature build-up: fumed silica, like all the other fumed metal oxides are produced in a very high temperature environment, so they are very stable under high temperature. However, as temperature of the coatings environment increases, particularly upon shear, wetting characteristic of the resin in the system typically improve. This can create a scenario for over-dispersion to occur. In this scenario, aggregates are reduced past their optimum association level, and reduced thickening efficiency results. A typical result of over-dispersion is minimal viscosity and thixotropic contribution, to the point where it appears no thixotrope or additive was included. Lastly, the point of sequence of addition, as fumed silica is one of the smallest particle size materials added. It is suggested to add early in the formulation, into preferably resin/vehicle, and not into non-film forming components. Caution should be used when post adjusting batches with powder, as often minimal shear is used which is inadequate for homogeneous incorporation. In this case, post addition with low shear might bring formulations into their rheological targets. However, the main indication of under dispersion is deteriorating stability over time, which occurs normally after short periods of hours or days.

Concerning use of fumed metal oxides in water based coatings, the main factors in the decision to consider a powder or pre-dispersed option is the intended dispersion method and into which liquid component it's intended to disperse the additive. Untreated and treated fumed silica, and to a certain extent alumina (in higher pH environments $\mathrm{pH}>10.4-12$ ), are efficient when it's possible to adequately disperse powder into water dispersible resins and solutions. Both untreated (200 $\mathrm{m}^{2} / \mathrm{g}$ ) and treated forms (DDS, HDS, HMDS treated, and $130-300 \mathrm{~m}^{2} / \mathrm{g}$ ) are found to be effective. For use of treated forms (when anti-corrosion improvement is also desired), resin solids should remain in the range of $35-40 \% \mathrm{NV}$. Incorporation of hydrophobically modified options becomes more difficult, when resin solids drop below this level.

When the intended purpose is to bring the additive into water directly, or into a shear sensitive film forming resin, then use of pre-dispersed forms of fumed silica is advised. Water, because of its low viscosity and high dielectric constant, has proved to be a poor grinding medium for fumed silica, making it difficult to achieve the degree of de-aggregation and dispersion of particles needed to achieve optimum benefits in water-based coatings. Pre-made dispersions of fumed silica in water however overcome these difficulties.

Lab evaluations have demonstrated that multiple performance attributes can be enhanced by the use of fumed silica dispersions such as, improvement of pigment, filler and matting agent suspension, reduced tack, improved dirt pick-up resistance, enhanced film strength, and even improved coalescence of some resins, without compromising gloss and other appearance attributes. The newest observations made in testing pre-made aqueous fumed silica dispersions is in the coalescence improvements in film forming resins without co-solvents / coalescing aides in some cases and with reduced levels in other cases. The net result is reduced overall VOC in addition to the properties discussed above. While further investigation into this behavior is ongoing, it is theorized that the interaction and uniform distribution of the of these finely dispersed fumed silica aggregates helps to orient the latex particles more evenly throughout the drying process, and helps coalesce into a high gloss dry film, without the use of co-solvent.


For more detailed information on rheology, optimizing dispersion and coalescence please see references $2,3,4,5,6,7$, and 11 . Resin and formulating details are furnished upon request.

## Anti-Corrosion / Water Repellency

Treated, hydrophobically modified grades of fumed silica have been used for decades along with anticorrosive pigments to improve corrosion performance and increase water repellency of coatings. Treated fumed silica are not considered anti-corrosion pigments, though work effectively with many classes of anti-corrosive pigments such as modified Barium Metaborate, Calcium Phosphosilicate and Zinc dust has been proven through many lab studies. The main GREEN coatings segments which have taken advantage of this traditional use are high solids, water and radiation cure systems, and the main key success factor is adequate loading level. To enhance this property, loadings of $>1.0 \%$ and $<3.0 \%$ by weight on total bring enough particles into a coating matrix to increase level of hydrophobicity enough resulting in improvement. Water repellency, corresponding to improved blister resistance is affected by lower loadings levels starting at $0.5 \%$ (by weight).


White Latex Primer with modified Barium Metaborate After 5 cycles alternating 100 hr Prohesion* salt spray and 100 QUV


Whether to improve anti-corrosion behavior or water repellency, proper dispersion is needed to homogeneously distribute aggregates throughout the coating matrix. For optimum performance, it is suggested that the treated fumed silica be added into the grind stage with the anti-corrosion pigments. Silane treatments of DDS, TMOS, HMDS on core particles ranging from 7-16 nm (corresponding to $300-130 \mathrm{~m}^{2} / \mathrm{g}$ surface area) are most typical. Hydrophobicity is ranked in ascending level with DDS $<$ TMOS $<$ HMDS, with HMDS treated silica being the most hydrophobic, only behind PDMS treated grades. As discussed, in previous sections though PDMS treated cores are most hydrophobic, care should be used in formulated them into coatings, as migratable silicone could negatively affect other properties such as adhesion. For more information on improving water repellency and corrosion protection, please see references 2 and 12.

## Scratch Resistance

Development of particles for the specific purpose of improving scratch resistance resulted from development of particles for high reinforcement of elastomers and composites. The critical success factor to achieve high reinforcement, beyond traditional levels, is to be able to fill polymer matrices with significantly higher levels of fumed silica, without generating high viscosity which negatively impacts application. The main process development to optimize particle design for use as a high reinforcing filler and to impart scratch resistance is structure modification through mechanical post processing. This results in a highly reduced structure and level of aggregation. The corresponding physical property observed is a significant increase in the bulk density and dramatically reduce capacity to increase viscosity.


The important factor for scratch resistance is being able to load polymer matrices up with higher loading levels of inorganic, slightly structured aggregates. Both inorganic classes of silica and alumina have been used to enhance scratch resistance, however silica has the advantage of a lower refractive index of 1.46 (where alumina is 1.7-1.8). This lower refractive index is more closely aligned with many polymeric systems which results in improved clarity. To reduce influence of the hydrophilic nature of fumed silica, particles used to improve scratch resistance are hydrophobically modified with DDS, HMDS and TMOS.

## Various Scratch Methods Used:



## Formulations and dispersion conditions used:

UV-Cure Guide Formulation*

| Mill Base* |  | weight \% |
| :---: | :---: | :---: |
| Laromere PE 44 <br> F | BASF AG | 68.0 |
| Tripropylene glycol diacrylate (TPGDA) | BASF AG | 32.0 |
| DDS treated. SMS, 12 nm | Evonik <br> Degussa <br> GmbH | 10.0 |
| Hardener |  |  |
| Darocur8 1173 | Ciba Speciaity Chemicals | 4.4 |
| Total |  | 114.4 |

2- Pack High-Solids Guide Formulation*

| Mill base ${ }^{\text {x }}$ |  | weight \% |
| :---: | :---: | :---: |
| Macrynal ${ }^{\text {P }}$ SM 565, 70 \% | Cytec Surface Specialties | 61.0 |
| Butyl acetate |  | 7.3 |
| Methoxypropylacetate |  | 1.7 |
| Solvesso ${ }^{\circ} 100$ | Exxon Chemical GmbH | 2.0 |
| Xylene |  | 2.7 |
| DDS treated, SMS, 12 nm | Evonik Degussa GmbH | 5.0 |
| Let Down |  |  |
| Desmodur ${ }^{\text {N }} 3390 . \quad 90 \%$ | Bayer Material Science | 22.3 |
| Butyl acetate |  | 2.0 |
| Solvesso ${ }^{\text {® }} 100$ | Exxon Chemical GmbH | 1.0 |
| Total |  | 105.0 |

* Dispersions conditions: 60 min Dispermat (pearl mill, with $0,5 \mathrm{~mm} \mathrm{ZrO}_{2}$ media)

The two important considerations for successful use of surface treated, structured modified fumed silica particles are adequate loading level and adequate shear rate (combined with small, hard media). Many trials have been conducted optimizing loading and shear and the critical factors learned are; intensive milling using Zirconium media of very small size $(0.5 \mathrm{~mm})$ is needed over longer periods of several hours. Optimum loading level starts at $5 \%$ by weight on total and can approach $15 \%$. Inorganic particle load must be high enough to attain a homogenous density throughout polymer to achieve a consistent, reinforced matrix. SEM analysis of a cross section of the high solids coating noted above shows a homogenous distribution through the film with no surface enrichment resulting from higher particle density.


In the high solids system tested, $5 \%$ loading of a structured modified $\mathrm{SiO}_{2}$ particle treated with DDS achieved improved scratch resistance, as tested by dry scratch method with Crock meter (abrasive paper) and wet scratching method by Elcometer ( 40 double strokes, bristle brush and $0.15 \%$ quartz in water slurry). Improved scratch resistance is observed through higher gloss
retention, after scratching based on the specific method. Reduced haze is also observed after test panels were subjected to Elcometer testing. Test panels showed a slight decrease to initial gloss and slight increase to haze with the addition of $5 \%$ additive, however significant improvement is observed on test panels after subjected to scratching via both scratch methods.

The last example demonstrates use of $8.7 \%$ structured modified, MEMO and DDS treated silica dispersed directly in a UV cured system (polyester acrylate-Laromer P44 and TPGDA (Tripropyleneglycoldiacrylate), and via a pre-dispersion of $30 \%$ silica in TPGDA first and then making final coating (photoinitiator-Darocur 1173) with paste instead of direct dispersion. Though two final coatings were made and tested with the structured modified, DDS treated silica (direct and via paste first), viscosity was prohibitively high and stability was poor. A sample made by direct addition of structured modified, MEMO treated silica was lower in viscosity, however stability was also poor. The sample which remained stable throughout testing and showed the best improvement to scratch resistance (with minimal contribution to haze) was the coating made with a pre-dispersion of structured modified MEMO treated silica and use of additive Tego LA-D 1045. For more detailed information on scratch resistance, see reference 8.

## Free Flow, Fluidization, Transfer Efficiency

The common bulk properties in the ever broadening powder coating field, whether they be conventional, fine, thermosetting, thermoplastic, tribo or UV cured are; all require good flow, reduced moisture pick-up, and good package stability (no caking). The common performance attributes desired in application are; efficient fluidization, high transfer efficiency to reduce waste and reduced faraday cage effects for even film thickness and optimized appearance. All four classes of untreated - hydrophilic, treated - hydrophobic fumed silica and alumina are used to achieve improved flow, stability with reduced moisture pick-up and improved fluidization and transfer efficiency. With recent particle developments of a high surface area alumina ( $130 \mathrm{~m}^{2} / \mathrm{g}$ ), and commercialization of alumina surface modified with TMOS, rendering it hydrophobic, further improvements are observed in conventional, fine and tribo applied powder coatings, in the areas of transfer efficiency and improved fluidization.

In practice, flow additives used in powder coatings can be added in one of three places in the powder coating manufacturing process; in hopper directly, dosed into powder during chipping and post added after pulverization. Flow additives can be dry blended into problematic powdered components prior to adding these components into the hopper, to help them feed more consistently and homogeneously into the extruder. Typical loading of additive to treat problematic powder components going into the hopper is $0.1-0.3 \%$. If flow additives are used to pre-treat components, they are extruded into the powder matrix and do not influence the bulk flow properties after the powder is compounded and pulverized. For additives to influence the final powder coating properties, they must be added after extrusion and be oriented on the outside of the powder coating particle. To orientate the additive outside, there are two places where silica or alumina (or combination of the two) can be added into the process; prior to chipping where the additive is actually cut into the powder coating particle or after pulverization and classification. Care should be taken when dosing the additive in before pulverization as classification systems can classify additive out of the powder and change the final level which actually remains in the powder coating. The typical dosage level used in the chipping or as post add is $0.1-0.3 \%$ by weight.

To assess specific performance attributes associated with four classes of additives, a contract study was organized with the University of Western Ontario testing these 4 classes of additives in 3 powder coatings. Of the three powder coatings tested, two were corona applied. The first was a coarse particle size (conventional), polyester with $d_{50}$ of 31.5 microns and the other was a fine particle size, polyester with $d_{50}$ of 21.5 microns. Dosage level of the additive was adjusted based on particle size of powder. A $0.3 \%$ dosage rate was used for the coarse powder and a $0.5 \%$ dosage rate was used for the fine powder. The third powder used was a tribo applied polyester powder coating. Attributes assessed in both the coarse and fine polyester powder coatings were
angle of repose (flowability), bed expansion (flowability \& fluidizability), powder transfer efficiency, Faraday cage effects, gloss and gel time.

As Alumina is often preferred in tribo applied powder coatings, due to its more neutral to slightly positive electrostatic charge character, only alumina was tested in the tribo applied polyester powder coating. Attributes assessed include: transfer efficiency and Faraday cage effects

Four types of silica were tested and 3 types of alumina were tested in the coarse and fine polyester powder and only 3 types of alumina were tested in the tribo applied polyester powder. The four types of silica included: $200 \mathrm{~m}^{2} / \mathrm{g}, 130 \mathrm{~m}^{2} / \mathrm{g}$-DDS, $300 \mathrm{~m}^{2} / \mathrm{g}$-HMDS, $200 \mathrm{~m}^{2} / \mathrm{g}+\mathrm{chrg}$ (double treatment of HMDS and aminosilane). The alumina types tested included: $100 \mathrm{~m}^{2} / \mathrm{g}, 100$ $\mathrm{m}^{2} / \mathrm{g}$-TMOS, $130 \mathrm{~m}^{2} / \mathrm{g}$.

Results from selected trials, assessing Transfer efficiency and Faraday cage effects, are demonstrated below where the resulting round disk applied with coarse powder with $0.3 \%$ high surface area alumina ( $130 \mathrm{~m}^{2} / \mathrm{g}$ ) has a more consistent level of jetness then the disk applied with the black powder, with no additive. This test measures how much powder is transferred to the disk (by weight) under controlled application conditions. Faraday cage effects are measured by how much coating is deposited in the inner trough of a test specimen, where the interior parts of the trough has 3 removal panels, under controlled applications conditions. After application, these panels are weighed and the amount of powder deposited in the interior trough is weighed. Reduced Faraday cage effect (improvement) is associated with higher, more consistent weight of powder deposited on the 3 inner removable panels. In this case, $0.3 \%$ alumina treated with TMOS was effective in reducing Faraday cage effects (improve performance) in the coarse black polyester powder coatings.

Fluidization efficiency is another attribute assessed in this study. The results in coarse and fine powder show that particle size of the powder coating significantly affects which class of additives is most effective to improve fluidization. The general trend shows that in the coarse powder coating, Alumina was more effective to improve fluidization, with lower air velocities measured to obtain $20 \%$ bed expansion and Silica was more effective in the fine powder coating. This trend may prove useful to powder coatings formulators dealing with decreasing powder coating particle size, which is an industry trend, and that additive packages may need to be adjusted based on their particle size.
Transfer Efficiency \& Faraday Cage Effects



Fluidization Efficiency
Air velocity $\mathrm{Ug}[\mathrm{cm} / \mathrm{s}]$, which is needed to obtain $20 \%$ bed expansion.


- Fine particle size powder coatings: $\mathrm{d} 50: 21 \mu \mathrm{~m} / 0.5 \%$ additive
- Coarse particle size powder coatings: $\mathrm{d} 50: 31 \mu \mathrm{~m} / 0.3 \%$ additive
- The air velocity of the controls without silica or aluminium oxide was $>0.5$ (course) and $>1.0 \mathrm{~cm} / \mathrm{s}$ (fine)

For more information and details on the use of fumed metal oxides in powder coatings and the full details of the study carried out, in conjunction with the University of Western Ontario, please see reference 9 .

## Transparent IR and Conductivity

The two main specialized coatings applications driving the high interest in ITO are coatings which are transparent and anti-static and those which are transparent and IR absorbing for glass, plastic and thin film substrates. Market interest is higher for anti-static coatings on plastic substrates and films, where charge build-up and discharge can be very problematic for electronic components. Also surfaces with high electrostatic charge are susceptible to more dust contamination. Interest for transparent IR absorbing coatings is higher for glass, plastic and thin films, where the need to reduce transmission of thermal radiation is high, while maintaining the benefits of day light wavelengths. Interest in these specialize coatings has increased specifically to reduce energy consumed for heating and cooling in enclosed areas and reduce heat build-up on surfaces where, heat stress may cause premature part fatigue and operation failure. Basic physical chemical properties are summarized below. Color is an indicator of quality. Blue color results from a post stabilization process, which results in the highest electrical conductivity. Yellow and gray forms of ITO have lower electrical conductivity. Temperatures $>200^{\circ} \mathrm{C}$, in the presence of oxygen, will result in loss of blue color and deteriorate conductive properties.

Table next to typical phys-chem property of ITO gives coatings details to 3 UV cured systems containing various conductive ITO grades commercially available on the market. This system is UV cured at ordinary atmosphere (no Nitrogen needed). The coatings were applied by down bar over PMMA substrates. The grey area contains data from Evonik Degussa supplied ITO. The dry film was $2 \mu \mathrm{~m}$. Conductivity tested to be $10^{\wedge} 6 \mathrm{Ohm} / \mathrm{sq}$. with $<0.9 \mathrm{~g} / \mathrm{m}^{2}$ ITO coverage rate. The ITO concentration in the final (dry) coating is between 30 and $35 \mathrm{wt} . \%$. The concentration in the wet lacquer is $7 \mathrm{wt} . \%$.

| Product Parameter | Unit | Typical value | Method |  | UV Lacquer | Japanese Competitor | European Competitor |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Powder conductivity | [ $\left.\Omega^{*} \mathrm{~cm}\right]$ | <2 | spec. Resistance at $1,6 \mathrm{~g} / \mathrm{cm}^{3}$ | Surface Resistivity (ohm/sq.) | $10^{5}-10^{7}$ | $10^{6}-10^{7}$ | $10^{6}-10^{8}$ |
| Particle size $\mathrm{D}_{50}$ | [ nm ] | $105 \pm 15$ | Horiba 500 PCS, N076 |  |  |  | $\xrightarrow{>75}$ |
|  |  |  | Horiba 500 PCS, N077 | Light Transmission (\%) | 89 | 80 | slightly blue |
| Particle size $\mathrm{D}_{90}$ | [ nm ] | $160 \pm 20$ | similar to N076 | Haze (\%) | <1 | <1 | < 5 |
| pH | 1 | 3-4 | $10 \%$ in water | Abrasion Resistance* |  |  |  |
| Specific Surface Area | m²/g | $45 \pm 15$ | DIN ISO 9277 | Haze \% | <2 | 26.51 | 13.55 |
| Color |  | blue | 1 | Abrasion** | $10^{7}$ | $10^{11}$ | $10^{12}$ |
| Tamped Density | $\mathrm{g} / \mathrm{l}$ | ca. 900 | N200 | Pencil Hardness | 3-5 H | B8 .. B7 | B8 |
| Chlorine Content | [ppm] | $\approx 1500$ | RFA | Sensitive against | NaOH | $\begin{gathered} \mathrm{NaOH}, \\ \text { Aceton, MEK } \end{gathered}$ | NaOH , <br> Aceton, MEK |
| Loss on Ignition | [\%] | $<2$ | N400 | Bending / Formability | no | yes | yes |
| Morphology |  | spherical aggregated crystalline particles (cubic $\ln _{2} \mathrm{O}_{3}$ ) | 1 | * Taber Abraser, 500 g <br> ** Scouring Test: Equip | cyles, PC <br> green pad 3 | 50 passes |  |

Optimized ratios of $\mathrm{In}_{2} \mathrm{O}_{3}: \mathrm{SnO}_{2}$ are available in powder forms, pre-dispersed in water, IPA, MEK, Ethanol, Propylene Glycol Propyl Ether and already formulated into conductive UV curable coatings. A summary chart below outlines typical thin film ITO coverage rates and surface resistivity as well as a IR absorbing spectrum of transparent, UV curable coating containing ITO ( 2 micron film thickness) applied over polymethylmethacrylate clear plaque. The chart next to it demonstrates the difference in temperature development over time when thermally cured acrylic coating applied over glass. The dry film thickness was $4 \mu \mathrm{~m}$ with an ITO coverage rate of $\mathrm{g} / \mathrm{m}^{2}$.


For more information on ITO details and use in coatings, please see reference 10.

## Summary and Conclusion:

Modified grades of fumed metallic oxides have been developed to improve a variety of performance attributes in the GREEN coatings segments. The major trend in recent years is to offer pre-dispersed forms to facilitate ease of use and avoid costly and time consuming grinding steps in water, solvents and most recently monomers. The following table is a quick summary of the performance attributes influenced for each coatings segment. The main points to note are pre-dispersed forms of fumed silica have been found to improve coalescence and reduce cosolvent levels, minimizing VOCs. Rheological contributions of powdered fumed oxides start out at loading levels $>0.5 \%$ by weight in liquid systems and little contribution is typically observed at lower loadings. Corrosion protection is loading level dependent and when usage rates are $<1.0 \%$, impact will not be significant. Hydrophobic, structure modified grades of fumed silica are effective to improve scratch resistance in high solids and UV cured coatings when adequate loading and shear are applied. Use of ITO is suggested for very thin film, non-pigmented coatings applications, where high transparency and optical clarity are requirements.


