“Functionalized inorganic polymer salts” as Charge Control Agents

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Abstract

The new class of “functionalized inorganic polymer salts” (FIP) provides Charge Control Agents (CCAs) that are synthesized from natural raw materials and that are heavy metal free. The concept of FIP will be described by the example of hydrophobically modified layered metal oxides (HMLM). HMLM-based charge control agents are colorless and consist of an inorganic backbone that is treated with organic counter ions. By variation of the counter ions these products can be modified for different toner systems. These can be classical physically prepared toners but also various chemically prepared toners. An overview of the chemistry of HMLM is provided and examples of HMLM-CCAs and their properties in the solid state and in dispersion are discussed.

Charge control agents for classical and chemical toners

A typical toner consists of a resin, colorant, charge control agent (CCA), wax and external additives. Important for print quality is adjustment of the toner to the correct triboelectric charge. CCAs increase the charge level, improve the quick charge up, stabilize the charge over time and reduce the humidity sensitivity.

More and more digital machines, which mostly require negative toners, have been replacing analog copiers / printers. The trend to color toners is now well documented. The requirements regarding environmental issues have been increasing, so that the focus of new developments is now on negative colorless environmentally friendly CCAs.

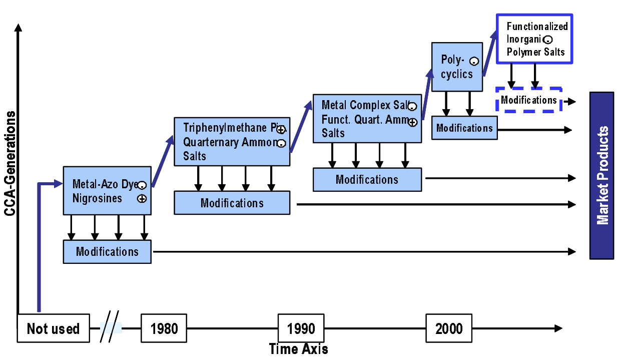

Fig. 1: Development history of CCAs

In addition to the classical toner production process, where all ingredients are dispersed into the toner resin, there are chemical toner processes that define additional requirements for modern CCAs, for example, compatibility with the chemical reaction used to form the toner particle.

The the latest innovation step in the development history of CCAs (shown in Fig 1) is a completely new chemical class which is a combination of organic and inorganic chemistry. This CCA family is named “Functionalized Inorganic Polymer salts” (FIP). Hydrophobically modified layered metal oxides (HMLM) are an example for this new chemical class of CCAs.

The concept of “functionalized inorganic polymer salts”

The inorganic / organic system approach offers a wide range of possibilities to adjust physical and chemical properties of the CCA toward the different toner systems and technologies.

There are two classes of “functionalized inorganic polymer salts”:

- Containing a cationic inorganic polymer
- Containing an anionic inorganic polymer

The tuning agent saturates the excess of cationic / anionic charge and can be either organic or an inorganic / organic combination.

The inorganic base components:

- are not based on heavy metals and contain no halides
- do not release VOCs
- contribute to lower CO_2 emission (as they are inorganic) and are not dependant on crude oil availability like pure organic systems.

While the inorganic backbone defines the rough charge level, final adjustment of the charge is controlled by the organic part. This is illustrated in Fig. 2:

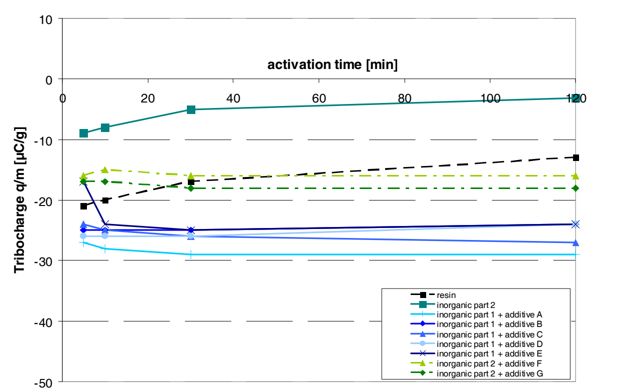

Fig. 2: Tribocharge of “functionalized inorganic polymer salts”: the inorganic part defines the rough level of charging which can be slightly adjusted by different organic tuning agents

Keeping the same inorganic backbone and changing the organic counter ion only slightly adjusts the charge magnitude, whereas use of a different inorganic base material leads to a material with different charging level. Fig 2 also illustrates that only the combination of inorganic base material and organic tuning agent results in reasonable tribocharging.

The organic part (tuning agent) also influences:

- Hydrophobicity
- Humidity stability
- Dispersibility in different media used in different toner processes

The concept of FIP will be described by the example of Hydrophobically Modified Layered Metal oxides (HMLM).

Hydrophobically modified layered metal oxides (HMLM)

Hydrophobically modified layered metal oxides are negative colorless charge control agents that can be used for both black and color toners. Two examples will be discussed: CCA 1 is an example of Type 1 HMLM (having an anionic inorganic backbone) and CCA 2 represents Type 2 HMLM (having a cationic inorganic backbone)[1].

Type 1(CCA1)	$[C]^{\oplus}_{org.}$ $[I]^{\ominus}_{oo}$	Organic cation / inorganic layered anion
Type 2 (CCA2)	$[I]^{\oplus}_{oo}$ $[A]^{\ominus}_{org.}$	Organic anion / inorganic layered cation

Particle size distribution

The width of CCA particle size distribution influences the ease of dispersion. Only optimum dispersion leads to a constant amount of CCA on the toner bulk surface[2]. Laser diffraction measurements show that both examples of HMLM (CCA 1 and CCA 2) have d_{50} values (agglomerates' average size) under 10µm. CCA 2 has a narrower particle size distribution than CCA 1.

Primary particle size

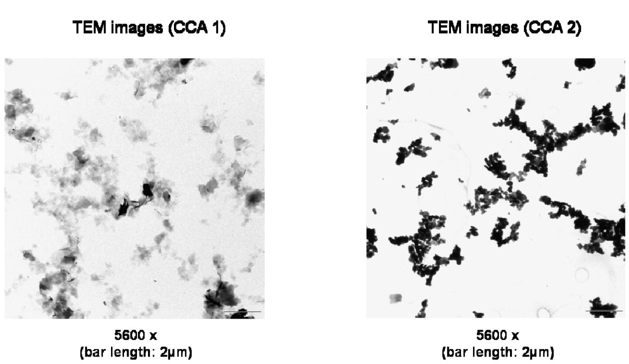

Fig. 3: TEM pictures of primary particles for CCA 1 and CCA 2

The primary particle sizes of typical CCA 1 and CCA 2 examples are shown in Fig. 3. While CCA 1 primary particle size is about 300-500 nm, CCA 2 has even smaller primary particles in the range of 100-200 nm.

A typical toner particle has a diameter of 5-8µm. That means that primary particles of CCA 1 and CCA 2 are 10-50 times smaller. Appropriate dispersing equipment allows the agglomerates to break apart so that submicron particle sizes can be reached easily as an optimum size close to the primary particle size.

HMLM - Thermal stability

HMLM–based CCAs have thermal stability exceeding 200°C, allowing common toner manufacturing to proceed without thermal decomposition.

Tribocharging behaviour of HMLM-based CCA (Type 1 and Type 2)

Dependence on concentration (in polyester resin)

At any concentration and for both types of HMLM-based CCA, a quick charge up can be observed. CCA 2 has a slightly higher triboelectric charge than CCA 1. Furthermore, an increase in tribocharge (in absolute values) is observed for higher concentrations of CCA. This dependence on concentration allows the adjustment of the tribocharging to a specific system by variation of the CCA amount.

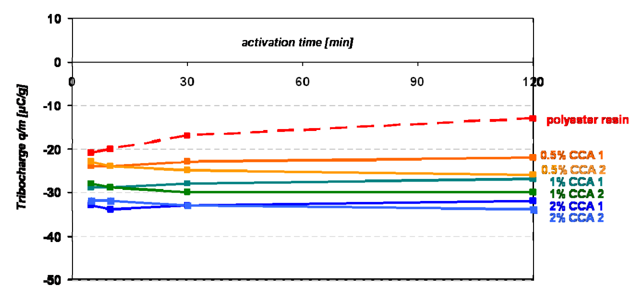

Fig. 4: Tribocharge behavior of CCA 1 and CCA 2

Comparison of HMLM – based CCAs to other chemical classes in polyester resin

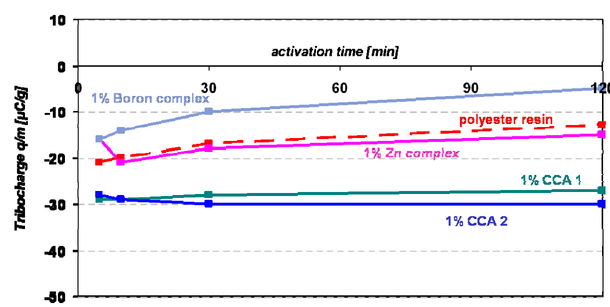

Fig. 5: Tribocharge of HMLM – based CCAs compared to other colorless CCA

In order to show the technical performance of the HMLM-based CCAs they have been tested against other negatively charging CCAs that are based on metal complexes. Fig. 5 clearly illustrates that CCA 1 and CCA 2 show quicker charge up, higher magnitude and better charge stability than the zinc and the boron complexes. Compared to the pure polyester resin, the zinc complex shows only a slight negative tribocharging. The boron complex shows the lowest charging behavior in this comparison.

Dependence on humidity in polyester resin

Fig. 6 shows the influence of HH conditions on the tribocharging of the two HMLM–based CCAs and a zinc complex when compared to the NN conditions. In all cases, a decrease (absolute value) of the tribocharge is observed. While CCA 1 and CCA 2 have comparable tribocharges at NN conditions (ca -30 µC/g), the Zinc complex has a lower one (-16µC/g). However, CCA 1 is more sensitive to humidity than CCA 2 and the Zinc complex. CCA 1 lost 60% of its initial tribocharge whereas CCA 2 lost ca. 30% and the Zinc complex 50%.

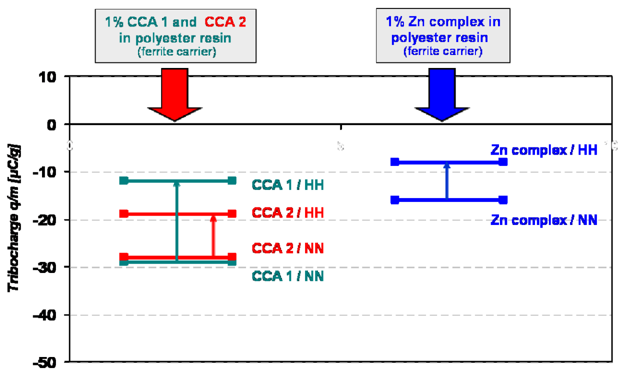

Fig. 6: Tribocharge at HH conditions and at NN conditions of HMLM – based CCAs compared to another chemical class of CCA

Combination with yellow pigment in polyester resin (colored test toner)

HMLM – based CCAs are colorless and therefore are suitable for color toners. Pigments have an influence on the toner charging depending on their chemical structure[3,4].

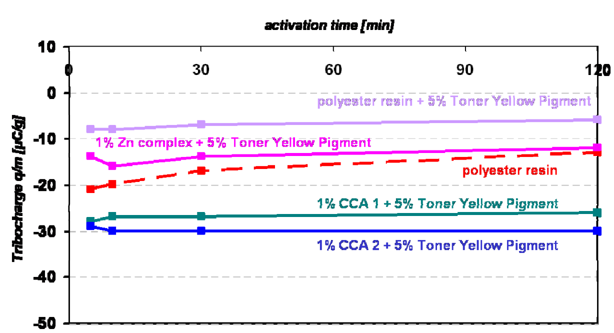

Fig. 7: Comparison of tribocharge in the presence of an Azo pigment between HMLM – based CCA and other chemical classes (in polyester resin)

Fig. 7 illustrates how the presence of a yellow azo pigment influences the charging behavior of test toners using different types of CCAs. Although the yellow pigment has a positive charging effect (relative to the resin), this effect is eliminated by the presence of the CCAs: the tribocharging of the test toners using yellow pigment plus CCA 1, CCA 2 or Zinc complex is comparable to the respective test toners without yellow pigment. Again – like in the case of the test toners without pigment- CCA 1 and CCA 2 provide more negative charging than the Zn complex CCA.

Styrene – acrylic systems

Most of the resins used for conventional toners are polyester. Many chemical toners on the other hand are styrene-acrylic based. HMLM-based CCAs also show good charging behavior in styrene acrylic resins.

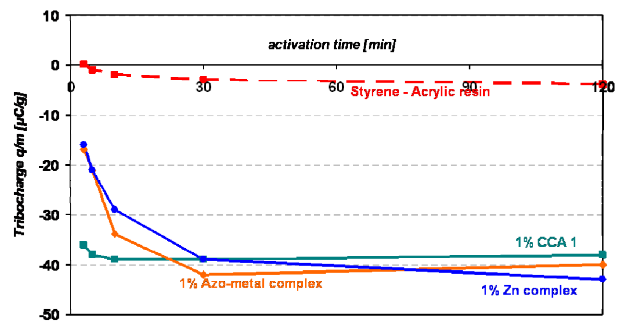

Fig. 8: Comparison of tribocharge in styrene–acrylic resin of HMLM – based CCA and metal complex based CCAs

Fig. 8 shows the triboelectric charging of CCA 1 and two other CCAs incorporated in a standard styrene–acrylic toner resin. The azo-metal complex is black and the zinc complex is a colorless CCA. After 2h activation, the q/m value is ca. -40µC/g for all CCAs tested. A quick charge up of CCA 1 can be observed in contrast to the other CCAs which need much more time before reaching a saturation value that they can then maintain.

Dependence of tribocharging properties on dispersion quality

In order to obtain the optimum charging properties with any CCA it is important to get the best dispersion of the CCA in the toner resin. The dependence of the tribocharging behavior on the quality of the dispersion is shown for CCA 2 as an example in Fig. 9.

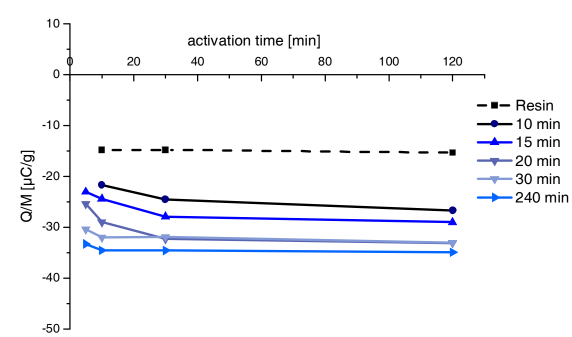

Fig 9: Dependence of charging behavior of CCA2 on dispersing conditions

If the CCA is dispersed only for a short time, the normal charge level of ca. -30 µC/g cannot be reached. In addition, the charge up time improves if the dispersion quality is better (dispersing time is longer).

Another method of getting a better dispersion quality is to prepare a CCA masterbatch, where the CCA is predispersed at a higher concentration and is diluted in the final toner making process. Fig. 10 shows the differences in charging behavior between a test toner having 1 % CCA dispersed either in a one step process (starting from powder) and two step process (dilution of 40% masterbatch).

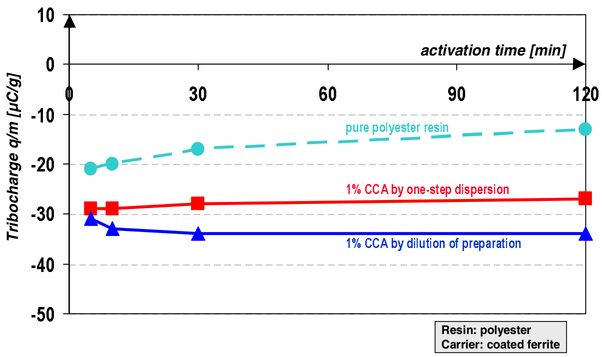

Fig 10: Dependence of charging behaviour of CCA 1 on dispersing conditions: one-step dispersion and two-step process using a predispersion

By using the masterbatch it is possible to obtain the final charging level even after a relatively short dispersing time (15 min) as the CCA is already fully dispersed in the masterbatch. Using CCA masterbatch may improve the toner quality without the need to extend machine time in the toner making process. This is a well established procedure in the pigment industry where pigment masterbatches (predispersed pigment concentrates) are used instead of pigment powders.

HMLM in chemical toners

As there are many different types of chemical toners, a CCA has to fulfill different requirements depending on the process that is used. For emulsion aggregation toners the CCA should be dispersible in water. For suspension polymerization toners the CCA should stay in the monomer phase and not go to the surrounding water phase.

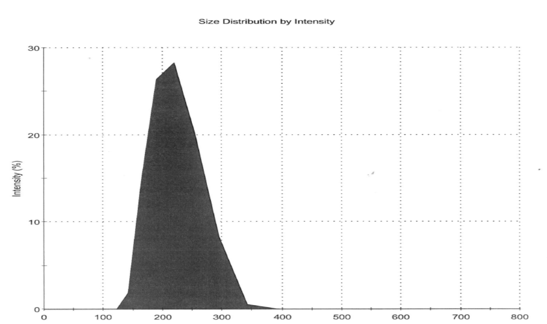

Fig. 11: Particle size distribution of CCA 2 in aqueous dispersion (15 % CCA 2)

In all processes the CCA should not interfere with the chemical process (e.g. inhibit the polymerization process). The concept of FIP offers the possibility to tune the properties of the CCA according to the respective toner process.

Fig 11 shows the particle size distribution of an aqueous dispersion of CCA 2 that could be used in a chemical toner process. The dispersion contains 15 % CCA 2 and has low viscosity. The particles are in the range of the primary particles.

Conclusion

The concept of "functionalized inorganic polymer salts" was described using two examples of hydrophobically modified layered metal oxides. HMLM are a new chemical class of charge control agents consisting of an inorganic backbone and organic additives (tuning agents). By variation of the backbone and the additives the charging behavior can be tuned for the respective application. The tuning agents in addition influence e.g. dispersibility, environmental stability or hydrophobicity. HMLM are environmental sound products that can be used in classical and chemical toners.

References

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Biography

Ulrike Rohr is Development Manager Toner in the group Technical Marketing Non-Impact Printing of the Division Pigment&Additives at Clariant Produkte (Deutschland) GmbH, Germany. This group markets products for NIP applications (toner as well as ink jet materials) and also deals with R&D for these products. Ulrike Rohr is head of a team focussing on R&D of materials for electrophotography like pigments, pigment preparations and charge control agents. She holds a Ph. D. in chemistry from Johannes Gutenberg-University, Mainz, Germany. Her doctoral studies were done at Max Planck Institute for Polymer Research, Mainz, Germany.

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