WHITE PAPER

THE BEST FOR RED AND YELLOW

A new additive technology for waterborne iron oxide pigment concentrates

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In decorative coatings, the use of pigment concentrates is a modern and flexible way to produce coloured paints. Especially in waterborne applications, these concentrates have to be suitable for a broad range of different binder technologies. Because of that, the concentrate formulations are usually free of binders and feature a broad compatibility. Furthermore, the demands in terms of storage stability, colour strength and cost efficiency are very high. These demands are addressed directly to the used additive technology. The additive has to induce outstanding viscosity reduction to achieve the highest pigment loads and the most economic grinding. It has to stabilise the pigments over a long period of time without any change in viscosity and it has to develop maximum colour strength to avoid any waste of expensive pigments.

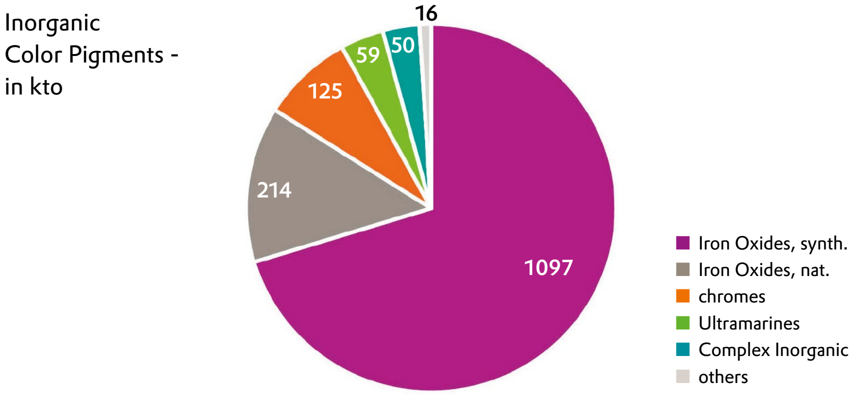
The most important pigment class in decorative coatings are the iron oxides. Iron oxides are not difficult to wet because of their shape. Iron oxide yellow tends to give dilatant rheology, which can be a disaster when it comes to automatically dosing in a dispensing machine. Iron oxide red, on the other hand, tends to increase the viscosity of pigment concentrates over time.

This paper elucidates to different structures of wetting and dispersing additives, which could be used in waterborne, binder-free pigment concentrates for iron oxides and their performance. It is focused on the stability and the wetting of the pigments, which are reflected by the viscosity reduction, the storage stability of the pigment concentrates and the colouristic properties. For the characterisation of the wetting behaviour and the dispersing efficiency, the zeta potential has been used. In the end, advice and guidelines for formulating iron oxide pigment concentrates will be given.

PIGMENT CONCENTRATE TECHNOLOGY

The dispersion of the pigments is the most extensive step during production of a coloured coating. For waterborne decorative coatings, typically, a white base paint is produced by direct grind and the colour is adjusted by using pigment concentrates. These pigment concentrates usually are prepared binder-free. The advantage of using binder-free pigment concentrates is the broad compatibility to different base paints. Beside titanium dioxide in decorative coatings, by far the

Figure 1. HS – Chemical Economics Handbook – Inorganic colour pigments consumption of inorganic colour pigments in 2014



biggest group of pigments are iron oxides. Pigment concentrates based on iron oxide yellow and iron oxide red are produced in large quantities. These are used for in-house tinting, as well as at the point of sale in tinting machines.

The target for the production of iron oxide pigment concentrates, especially for in-house tinting, is to achieve a maximum pigment loading to reduce the effort in the production. The biggest challenge is to stabilise the pigments in the liquid phase and, thereby, achieve a very good longterm stability without any settling. The fact that iron oxides have a very high density makes this step a tough job. It is a tough but beneficial challenge to have a low viscosity, free flowable pigment concentrate.

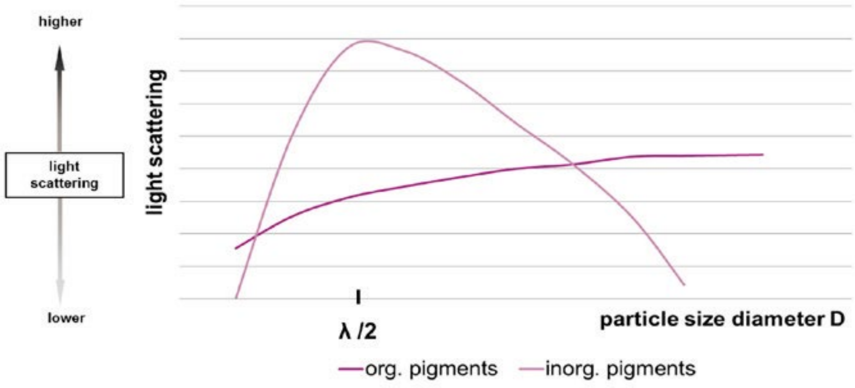
PIGMENT DISPERSION PROCESS

In the first step of the dispersing process, the surface of the pigments has to be wetted by a liquid. This means the air on the surface and in the pores of the pigment have to be replaced by wetting and dispersing an additive. According to the Young-equation ($Y_s = Y_{sl} + Y_l \times \cos \Theta$), it can only happen when the surface tension of the liquid is lower than the surface energy of the pigment. During the wetting process, the additive adsorbs on the pigment surface and creates new interfaces. The interactions of the pigment particles among themselves, which are generated by van-der-Waals forces are decreased and the viscosity of the dispersion is reduced. The viscosity reduction in the grinding stage is the first indication of successful pigment wetting.[1]

The target of the dispersing process is to achieve very small particle sizes with a large surface area, which leads to higher colour strength and good hiding power. During the grinding stage, the pigment agglomerates are broken down mechanically, ideally to primary particles. Newly created surfaces also have to be wetted by an additive.

The hiding power of pigment particles determined by light scattering is related to the particle size. Inorganic pigments show a maximum in light scattering at a particle size of half of the wave length of the scattered light (λ/2).

Figure 2. Relationship: Light scattering – particle size diameter[3]

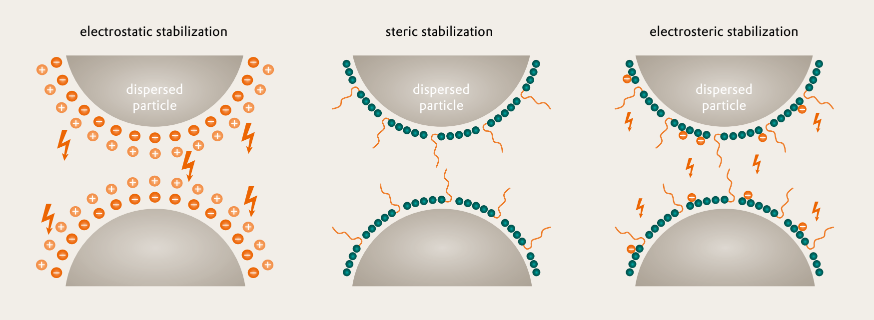


The third step of the dispersion process is the stabilisation. To achieve a good stabilisation of the pigments, the wetting and dispersing additive first has to adsorb on the surface of the pigment. Therefore, the additive requires anchor groups with high affinity to the pigment surface. In the case of iron oxide pigments, the additive should have pigment affinic groups, which are able to build up hydrogen bonding or dipole-dipole forces with the surface of the pigment. Most suitable functional groups for a good adsorption on iron oxides are hydroxyl-, carbonyl- or carboxyl groups.

THE STABILISATION OF THE PIGMENTS CAN BE CARRIED OUT ACCORDING TO THE FOLLOWING MECHANISMS (FIGURE 3):

- Electrostatic stabilisation
- Steric stabilisation
- Electrosteric stabilisation

Figure 3. Mechanisms of pigment stabilisation[4]



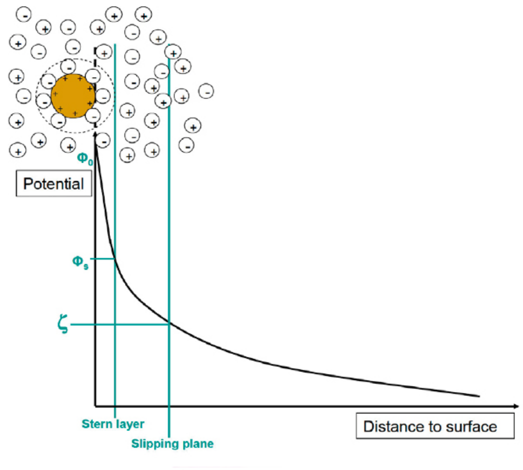
The most important stabilisation mode in waterborne formulations is electrostatic repulsion. In the ideal case, the wetting and dispersing additive, which is adsorbed on the pigment surface dissociates into an anionic and a cationic part. The cationic counter ions form a mobile diffuse cloud around the pigment particle, which leads to an electrostatic double layer. The electrostatic repulsion stabilises the particles against flocculation.

ELECTROSTATIC STABILISATION – ZETA POTENTIAL

The effectiveness of the additive regarding the electrostatic stabilisation can be described by the zeta potential ζ. The first adsorption layer with negative charges is generated by the wetting and dispersing additive but not the whole charge of the pigment particle is compensated. A second diffuse layer with a diffuse charge distribution is built up predominantly with counter ions. Both layers represent the electrostatic double layer (ion cloud).[2]

The surface potential cannot be determined directly and, therefore, the zeta potential is measured. In this case the migration speed of the particles in an electrical field is evaluated. When electrostatic charged particles move in an electrical field, they take a part of the ion cloud with them. The higher the distance of the ions to the pigment surface, the lower the interaction with the pigment surface.[2]

Figure 4. Mode of electrostatic stabilisation



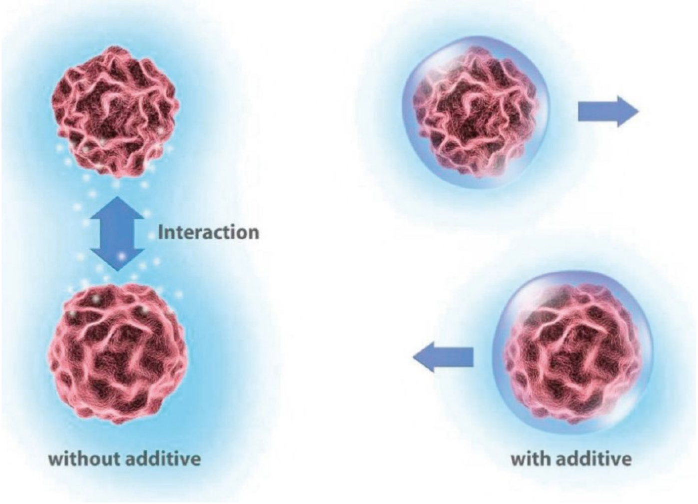
The loosely bound diffuse layer shears off and the potential at this shear plane is termed zeta potential. The higher the zeta potential, the better the stabilisation of the pigments. This potential can be measured electro-acoustically. The advantage of this method is that it can also be used in concentrated dispersions. In contrast, optical methods can only be used in diluted systems. By titrations with additive or pH titrations, interactions between pigments and additives can be characterised and so the electrostatic stabilisation can be described.

The zeta potential does not describe the steric stabilisation, which is another important mechanism in waterborne formulations. The steric stabilisation is not achieved by ions and, therefore, no potential can be measured.

STERIC STABILISATION

As before, the anchor group of the wetting and dispersing additive adsorbs on the pigment surface. In contrast to the electrostatic stabilisation, here polymeric side chains are necessary.

Figure 5. Interaction between pigment particles with and without additive



These side chains must be soluble in the surrounding medium. When the pigment particles come closer to each other, the polymeric side chains of the additive give steric hindrance. The restriction of the freedom of movement leads to a lower entropy level and, thereby, induces an energy barrier between the particles.

One important effect of the stabilisation is the reduction of interactions between the pigment particles that would otherwise cause flocculation. These interactions also restrict the movement of the particles and give rise to the viscosity. The better the stabilisation, the lower the interactions and therefore, the viscosity.

DISCUSSION OF THE RESULTS

Table 1. Tested formulations

	PY 42 (%)	PR 101 (%)
Water	38.4	32.9
Dispersant	5.5	6.0
Pigment	55.0	60.0
Biocide	0.1	0.1
Defoamer	1.0	1.0
Additive solid on pigment	10.0	10.0

Typical formulations of waterborne binderfree pigment concentrates for iron oxide yellow and iron oxide red were used to prepare different pigment concentrates. Three different polyacrylate salts, one highly polymeric additive and a new additive have been tested.

PARTICLE SIZE AND HIDING POWER

The prepared colourants were let down with a styrene acrylic emulsion. Draw downs on black and white carton boards were prepared. The hiding power was determined by measuring the delta E value between draw downs over white and draw downs over black. The lower this delta E value, the higher the hiding power.

In addition the particle size distribution was measured using dynamic light scattering (MicroWave by MicroTrack).

Table 2. Particle size and hiding power

ADDITIVE	PARTICLE SIZE MI (NM)	Δ E
New additive	316	18.08
Polyacrylate	530	19.65

With the new additive, the particle size of iron oxide yellow was close to the optimum ($\lambda/2$). In this case, the highest hiding power could be achieved.

VISCOSITY AND STABILITY

The viscosity of the pigment concentrates was measured 24 hr after preparation and two weeks after storage at 50°C. A cone plate rheometer was used for the measurement. The polyacrylate salts showed useful results with both PY 42 grades. The polymeric additive and the new additive exhibited a stronger viscosity reduction. One of the polyacrylates did not give a stable viscosity over time. The other additives showed stable viscosities without settling.

For PR 101, more diverse results were obtained. Only one of the tested polyacrylates could achieve a processable viscosity, which increased significantly after storage. The polymeric additive and the new additive achieved much lower viscosities but only the new additive gave stable viscosities over time. See Figure 6.

Figure 6. Initial viscosities of the pigment concentrates

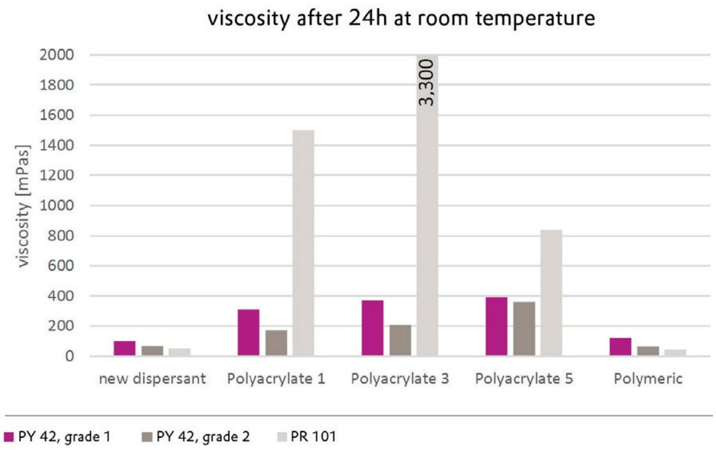


Figure 7. Zeta potential – iron oxide yellow

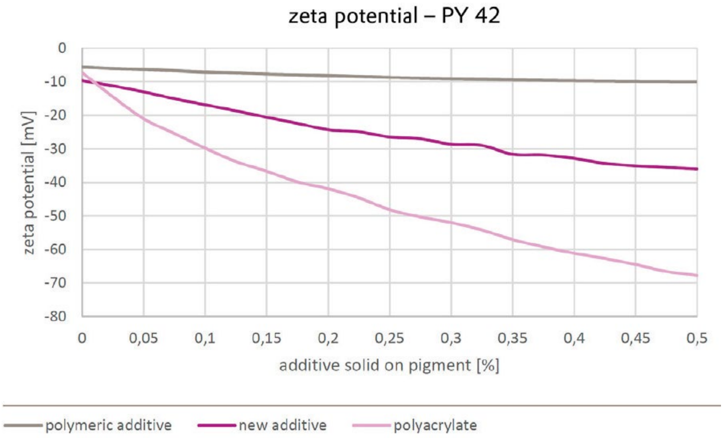
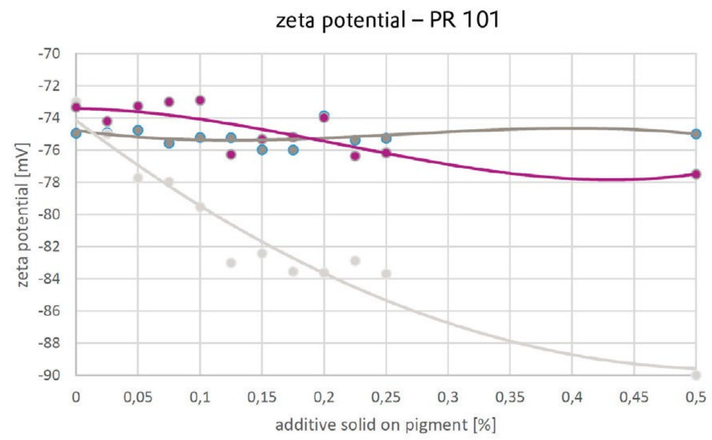


Figure 8. Zeta potential – iron oxide red



ZETA POTENTIAL

The zeta potential was measured in a 5 % pigment slurry. The respective additive was titrated until a constant zeta potential was reached. The highest influence on the zeta potential could be seen with an additive addition up to 0.5 % solid on pigment. The lowest zeta potential was achieved with polyacrylates, which reflects that the strongest electrostatic stabilisation could be achieved by using this chemistry. As expected, the non-ionic highly polymeric additive had almost no influence on the zeta potential. This additive class provides no contribution to electrostatic stabilisation. The zeta potential achieved by the new additive was in between the one by polyacrylates and the one by the polymeric additive. See Figures 7 and 8.

Figure 9. Stabilisation of PY 42

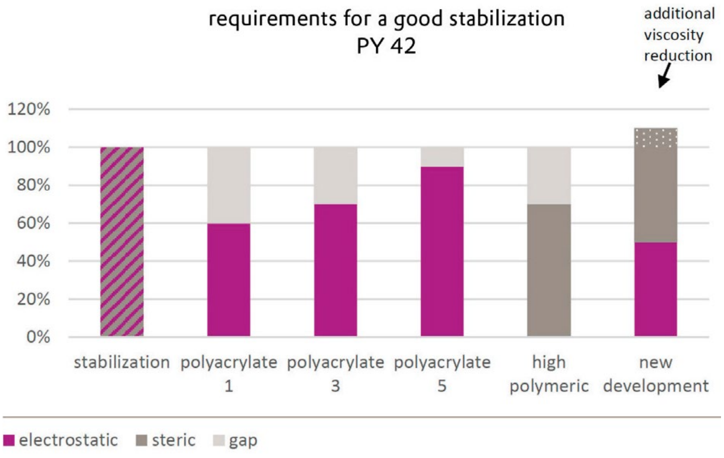
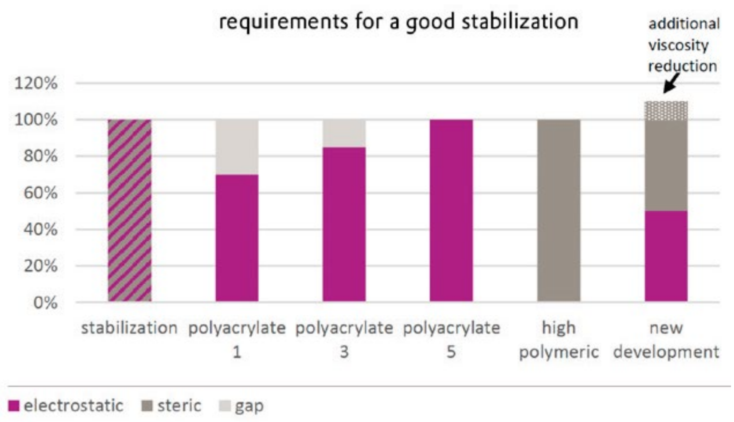


Figure 10. Stabilisation of PR 101



It is obvious that the zeta potential alone is not sufficient to interpret the results obtained by viscosity and stability measurement completely. The zeta potential does not give information about the steric stabilisation of the pigment particles. Providing that the steric stabilisation contributes beneficially to the performance, the results can be interpreted as follows. See Figures 9 and 10.

To stabilise the iron oxide particles, a certain amount of stabilisation energy is needed. Not in all cases can this amount of energy be provided by electrostatic energy alone. For those cases, additional steric stabilisation is necessary.

Furthermore, the newly developed additive did not only outperform the conventional technologies but provided the additional benefit of significant viscosity reduction as shown in the graph.

CONCLUSIONS

The results show that the new additive performs on a very high level with a broad range of iron oxide grades independent from their morphology and structure. It combines outstanding viscosity reduction and very good long-term stability of iron oxide concentrates with excellent hiding power. The new additive provides an optimised balance between electrostatic and steric stabilisation making it a very efficient additive. This additive helps to reduce complexity and finally it contributes to a more cost efficient way to formulate decorative coatings.

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