PAINTING A MORE STABLE PICTURE

Improving pigment dispersion and paint performance with versatile amino alcohols. By Dr Romain Severac and Yoann Fernandes, Angus Chemical Company,

Alkanolamines, such as 2-amino-2-methyl-1-propanol (AMP) and 2-amino-2-ethyl-1,3-propanediol (AEPD), are commonly used as key stabilising agents in a wide range of water-borne paint formulations. Not all alkanolamines are equivalent but AMP and AEPD can be used to improve the pigment particle size distribution and exploit synergistic effects with common dispersing agents. Optimising the formulation in this way has the potential to reduce raw material costs while improving paint performance.

One the most crucial steps in paint manufacturing is the dispersion of pigments, which drastically impacts almost all performance aspects of both the coating and dry film. The selection of a regular dispersing agent mixture usually depends on the composition of the pigment blend [1]. This is due to the variety of pigments and their chemical compositions, as well as the development of a wide range of surface treatments [2]. With the presence of the amine function and the alcohol group, alkanolamines can form both ionic and hydrogen bonds with the surface of pigments [3], which drives both the wettability of pigment agglomerates and the reduction of attractive forces between the particles resulting in the breakdown of pigment agglomerates. In addition, AMP or AEPD interacts with conventional anionic dispersing agents such as polyacrylic surfactants or polyphosphates. Modifying the nature of the counter ion of these polymeric species adjusts affinities with pigment surface. The combination of these specific synergies leads to an improved particle size distribution of pigments.

AMP ADSORPTION LINKED TO PARTICLE SURFACE

As shown in *Figure 1*, the adsorption ratio of AMP at the surface of several pigments was measured. The protocol used in this investigation is based on the preparation of slurries of each individual pigment at about 60 wt% solids content, with a disperser at high shear (20 min at 1700 rpm) in the presence of several concentrations of AMP. After this dispersing step, slurries are centrifuged (min. 2h30 at 4500 rpm) until the dispersed pigments are fully settled, and the unabsorbed amount of AMP, free in the filtrate, is determined by a straightforward titration with a strong acid. All raw materials were used as supplied.

The adsorption of AMP is significant in all cases (*Figure 1*) and this is important evidence of the strong affinity driving this phenomenon. The adsorption reaches a plateau that corresponds to the saturation of the surface.

The quantity of adsorbed products appears to be linked to the particle diameter. Given equivalent porosity, smaller particles have a higher surface area that can adsorb a higher concentration of AMP.

By using the same protocol, five slurries of titanium dioxides were prepared with a wide range of surface treatments (0.1% to 10.3% of SiO_2, 2.1% to 4.0% Al_2O_3, 0.0% to 0.5% ZrO_2, and up to 0.25% organic treatment). The adsorption of amino alcohols was standardised by dividing the molar adsorption by the TiO_2 surface areas. The versatility of the adsorption is confirmed as adsorption occurs whatever the TiO_2 treatment (*Figure 2*). The differences shown between the level of

RESULTS AT A GLANCE

→ Alkanolamines, such as 2-amino-2-methyl-1-propanol (AMP) and 2-amino-2-ethyl-1,3-propanediol (AEPD), are commonly used as stabilisers in water-borne paint formulations.

→ Depending on the chemical structure, agglomerates and particle size distribution can be optimised by exploiting specific amino alcohols and their interaction with pigments and dispersing agents.

→ Formulators can use amino alcohols to minimise undesirable side effects and improve overall pigment efficiency and potentially reduce costs.

→ Wet abrasion resistance is one example where amino alcohols and their synergy with common dispersing agents can improve paint performance.

the saturation plateau are close to the accuracy of the methodology and are insignificant.

IMPROVING TIO_2 DISPERSION FOR BEST LIGHT SCATTERING EFFICIENCY

In parallel, means of particle size (PS) have been determined using a laser scattering technique. The evolution of the PS means as a function of both AMP and AEPD concentrations is shown in *Figure 3*. The correlation between the concentration of both amino alcohols and the improvement in the TiO_2 dispersion applies to almost all TiO_2 types. This correlation is not visible with TiO_2 "Kronos 2043" or TiO_2 "Ti-Pure 706" as even at the lowest dosage (0.25 wt% of alkanolamines per pigment weight), the particle size is at the plateau. Further investigation will be performed at lower concentrations of these dispersing agents. In *Figure 2*, these two examples correspond to pigments with the highest affinity with AMP and AEPD (the adsorbed amount is the highest). Confirmation of the fundamental difference between a neutraliser, such as sodium hydroxide, and stabilisers, such as AMP or AEPD, may be seen in *Figure 4*. According to this experiment, showing the evolution of the TiO_2 particle size, shown as a function of dispersion time (66 wt% TiO_2, 1.5% of neutraliser, disc diameter 4 cm, can diameter 7 cm, speed 1600 rpm), either AMP or AEPD are able to wet and support the dispersion of TiO_2 which makes it possible to recover the expected optimum particle size and results in the best light scattering efficiency. At the opposite end of the spectrum, a simple neutraliser such as sodium hydroxide, even after a long dispersion time, is not able to significantly support this process.

AEPD REDUCES THE NEED FOR DISPERSING AGENTS

In addition to the natural dispersing property of both AMP and AEPD, the interaction with regular dispersing agents commonly used in the industry was evaluated [4]. *Table 1* presents a select list of dispersing agents containing polyphosphate and either a hydrophilic or hydrophobic, neutralised copolymer of maleic anhydride. Samples of copolymers were classified from the most hydrophilic (Sample 1) to the most hydrophobic (Sample 5). Dispersing agents have been engaged in dispersing agent demand curves (evolution of Krebs viscosities with dispersant concentrations) either alone or combined with AEPD. This common procedure consists of determining the minimum concentration of dispersing agent required to produce the optimum wetting point. This point corresponds to the concentration at which the viscosity no longer decreases.
Figure 5 sums up all comparative examples, and the impact of the presence of 0.3 wt% AEPD on these dispersing agents is significant. The systematic improvement of the dispersing agent shows the universality and versatility of AEPD. It means that the use of AEPD enables the reduction in primary dispersing agents in water-based formulated products, minimising drawbacks of these hydrophilic anionic species [5, 6].

LOW CONCENTRATIONS MINIMISE COMMON SIDE EFFECTS

In addition to the ability of minimising the overall dispersing agent concentrations to reduce the dry-film hydrophilicity, the strong inter-

Figure 1: Adsorption of AMP at the surface of several pigments.

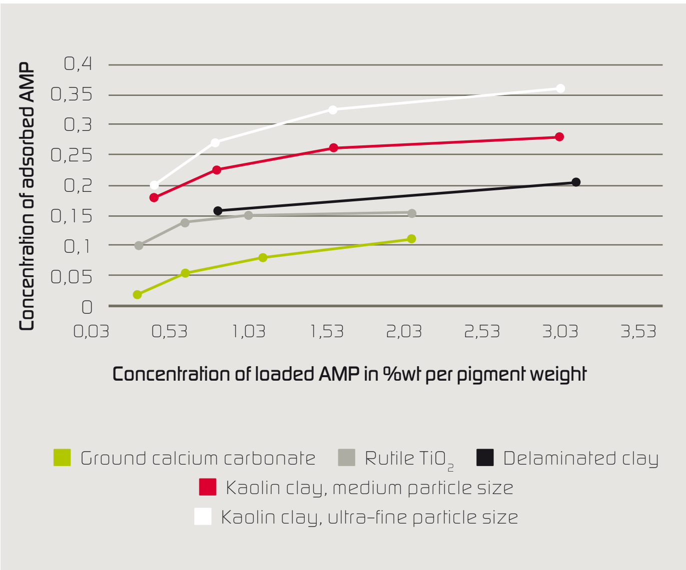
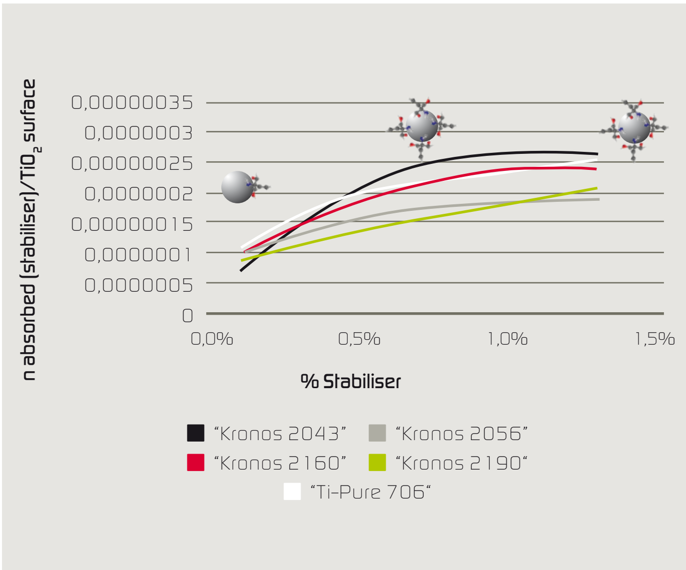


Figure 2: Adsorption average of AMP and AEPD at the surface of several TiO_2 particles.



action between AMP and AEPD with an acrylic dispersing agent can improve its intrinsic property. A set of satin water-based coatings with low volatile organic compounds, were taken through a design of experiment methodology (4 concentrations of TiO_2 from 12% to 18%; three neutralisers including AMP, AEPD and NaOH; and three concentrations of polyacrylic dispersing agents). Wet scrub resistance tests, based on the ISO 11998:2006 standard, were performed under harsh conditions (1500 cycles, 4 weeks of dry film drying, 200 µm applied on a panel, 4 repeated tests). *Figure 6* shows the statistical analysis in a box plot representation. Despite the lower concentrations of these additives, in the range of 0.1 wt% to 0.3 wt% loaded at the dispersion step, this experiment provides a good illustration of the result of the interaction provided by these amino alcohols. This effect could be also linked to the initial adsorption mechanism disclosed in this paper. As amino alcohols such as AMP or AEPD are adsorbed to a large extent on both pigments and fillers surface, and linked to dispersing agents, this reduces the remaining free amino alcohols in the binder matrix, minimising the well-known usual effect of highly polar compounds in a dry paint film. This effect becomes especially significant when considering the current reformulation trends for titanium dioxide optimisation, which leads to an increase of filler concentration that negatively affects this parameter if not properly adjusted.

Figure 3: Evolution of the particle size means of TiO_2 slurries containing AMP and AEPD.

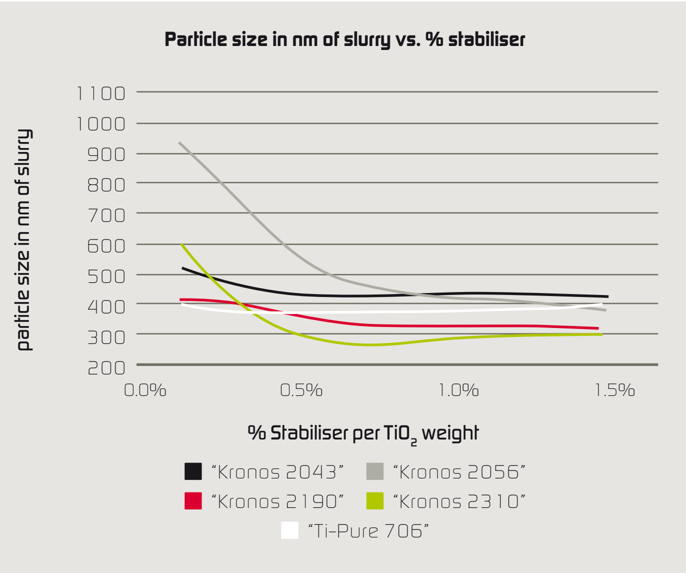


Figure 4: Evolution of particle size of TiO_2 Kronos 2190 slurries as a function of the dispersing time with difference neutralisers.

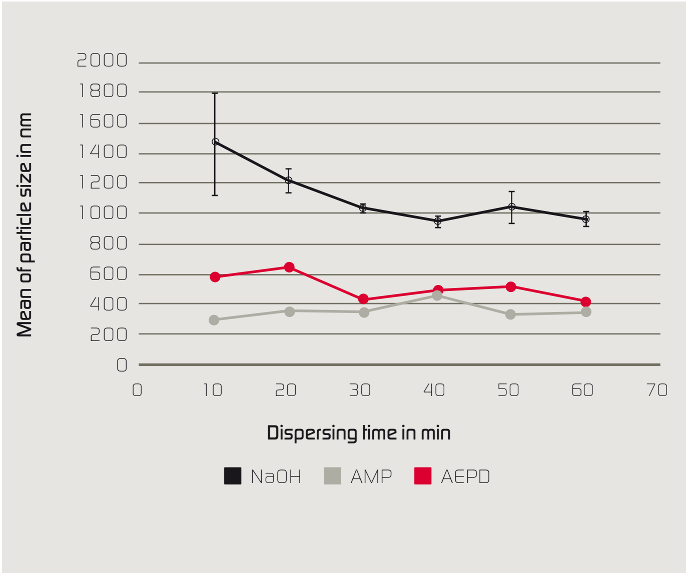
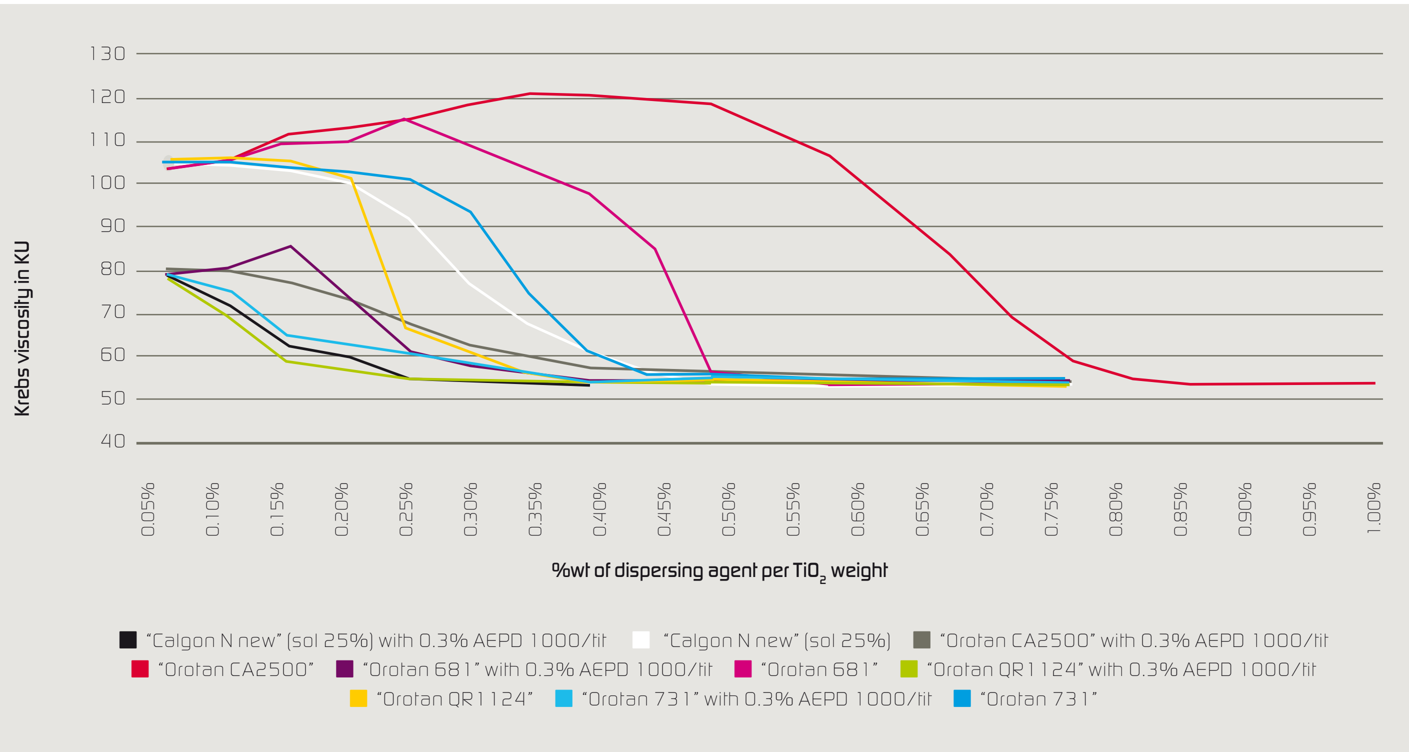


Figure 5: Dispersant demand curves with several dispersing agents and TiO_2 D with and without 0.3 wt% AEPD.



AMINO ALCOHOLS BOOST PIGMENT EFFICIENCY

Alkanolamines such as 2-amino-2-methyl-1-propanol (AMP) and 2-amino-2-ethyl-1,3-propanediol (AEPD), are commonly used as key stabilising agents in a wide range of water-borne paint formulations. Due to the strong interaction between specific amino alcohols and both pigments and dispersing agents, the level of agglomerates and the overall particle size distribution of pigments can be improved in paint formulations. Not all alkanolamines are equivalent, and these effects strongly depend on the chemical structure of the product. In addition to the natural dispersing ability of these molecules, synergistic effects have been identified with regular dispersing agents, such as polyphosphates and neutralised copolymers of maleic anhydride. The versatility of 2-amino-2-methyl-1-propanol and 2-amino-2-ethyl-1,3-propanediol can be used to reduce both numbers and levels of some commonly used paint additives through the optimisation of paint formulations, potentially lowering raw material costs while improving paint performance. Formulators are able to unleash the potential boosting effect of amino alcohols to significantly minimise the undesirable "side effects" of regular additives, and improve the overall pigment efficiency. In particular, the improvement of wet abrasion resistance can be enhanced by the presence of amino alcohols and thanks to synergistic effects with common dispersing agents.

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Table 1: Selected dispersing agents.

Dispersing agents	Technology	Neutralisation
"Calgon N*"	polyphosphate	sodium salt
"Orotan QR 1124*"	hydrophobic copolymer of anhydride maleic	ammonium salt
"Orotan 731*"	hydrophobic copolymer of anhydride maleic	sodium salt
"Orotan 681*"	hydrophobic copolymer of anhydride maleic	ammonium salt
"Orotan CA2500*"	hydrophobic copolymer of anhydride maleic	sodium salt

* Registered trademark of a third party

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"Formulators can minimise several negative side effects."

3 questions to Dr Romain Severac

Concerning the cost reduction: what would be your estimate in a standard formulation for a premium indoor paint? *We've seen in a number of formulations how the functional versatility of our amino alcohols can help formulators reduce both the number and levels of commonly used paint additives. For example, as demonstrated in this investigation, the highly effective co-dispersion properties of AMP or AEPD can enable the reduction of primary dispersing agents used in the grind phase. At the same time, the hiding and gloss performance of AMP and AEPD also imply a potential for reducing the use of both pigments and binders. The unique nature of our amino alcohols can enhance the long-term stabilisation of the coating system, which is primarily based on the pH buffering effect combined with the enhancement of regular dispersing agents (such as polyacrylates), improving the robustness, the reproducibility, and the shelf life of the formulated product. In addition, numerous studies demonstrate a potential synergistic effect between both AMP and AEPD and certain approved biocides in many formulation types across multiple applications. This synergistic effect can provide enhanced syneresis control and improved in-can stability, while helping formulators optimise their use of approved biocides, depending on the individual formulation.*

Which side-effect is minimised the best by using AMP and AEPD? *Because the versatility of AMP and AEPD may enable the significant reduction of commonly used primary dispersing agents, formulators can also minimise several negative side effects of these additives, such as water resistance or wet scrub resistance. In the case of reducing polyphosphates concentrations, the optimisation of these wetting agents helps to improve the overall rheology profile of the formulation. It is also important to stress that, as is with all dispersing agents, the optimum performance can be achieved by finding the right balance between the use of different dispersing agents.*

How can AMP and AEPD be implemented into an established formulation? *This is strongly driven by what individual performance improvements or attributes are being targeted with the formulation. To start, AMP or AEPD can be loaded, even partially, to enhance dispersion during the grind phase, especially when prepared as a solution of pre-neutralised blend of dispersing agents. This will enable AMP or AEPD to interact with the dispersing agent and, as a result, enhance the synergistic effect. Then, step by step, dispersing agents can be reduced until all desired critical performance properties are maintained.*

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REFERENCES

[1] Tiarks F., Frechen T., Kirsch S., Leuninger J., Melan M., Pfau A., Richter F., Schuler B., Zhao C.-L., Formulation effects on the distribution of pigment particles in paints, Progress in Organic Coatings 48 (2003) pp 140–152
[2] Winkler J., Dispersing Pigments and Fillers, (Hanover: Vincentz Network, 2012), p. 35.
[3] Müller B., Poth U., Coatings Formulation, 2nd revised Edition (Hanover: Vincentz Network, 2011), p. 172.
[4] Clayton J., Pigment/Dispersant Interactions in Water-based coatings, Surface Coatings International 9 (1997) pp 414–420
[5] Verkholantsev V. V., Multifunctional aids, European Coatings Journal, 5 (2000) pp 42–50
[6] Muth M., Freytag A., Conrad M., Maintaining protection: how dispersants affect corrosion resistance of waterborne paints, European Coatings Journal, 1 (2016) pp 30–33


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