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KEEPING UP THE SUSPENSION

Novel bio-based neutralising agent for fumed silica dispersions. By Peter Klug, Jörg Rüger, Clariant Germany and Silvia Ziebold, Clariant Switzerland.

Dispersions of fumed silica must be neutralised in order to maintain stability in water-based coatings. Common stabilisers fail to comply with several eco-labels. Dimethyl glucamine offers a completely safe and largely bio-based alternative. Rheology studies showed that it performs at least as well as DMEA.

Today, indoor home environments are polluted by an accumulation of molecules generated by outside air, solvents, tobacco smoke, biological pollutants such as mites, allergens and moulds, and building materials. People are subjected to two to five times more contaminants indoors than outdoors [1].

Experience and measurements show that the levels of indoor pollution, and specifically levels of heavy metals and particulate matter (PM), are higher than the average allowed by the World Health Organisation, all over the world. This is particularly concerning given that we now spend up to 90% of our time indoors [2].

For the coatings industry, an increasing consumer focus on creating healthier indoor surroundings means that high-quality water-based paints with a low VOC content are in demand. More broadly, a World Paint & Coatings Industry Study [3] forecasts water-based coatings gaining share over solvent-borne products in virtually all world markets.

Growing regulatory attention surrounding paint ingredients adds to concern. Because it can be difficult to understand the different critical substances in paints, consumers must rely on ecolabels in their buying decisions. With currently available raw materials and additives, formulators must therefore consider not only function but also the environmental profile when it comes to selecting paint ingredients.

From their perspective, additives should be multifunctional and universally applicable in order to reduce formulation complexity, raw material handling and logistics costs. In addition, they need to comply with increasing safety and environmental regulatory requirements.

THE VALUE AND PROBLEMS OF FUMED SILICA DISPERSIONS

Fumed silica dispersions are primarily added to control the rheology of liquid paint systems such as low PVC water-based paints, especially lacquers and varnishes. In addition to generating structural viscosity and behaving as an anti-settling agent for pigments, highly dispersed silica has been repeatedly shown to positively influence the mechanial properties of paint and coating films [4].

For example, it can improve mechanical strength and scratch resistance and increase hydrophobicity, which assists in improving corrosion resistance. Typically, the higher the loading level used, the more noticeably these attributes can be improved [5].

Dispersions are preferred by the industry because of their easy handling. They are easily pumpable and are dust-free. In order to create storage-stable fumed silica dispersions, a suitable neutralising agent is necessary.

Figure 1a: Particle size distribution of the fumed silica slurry dispersions stabilised with dimethyl glucamine.

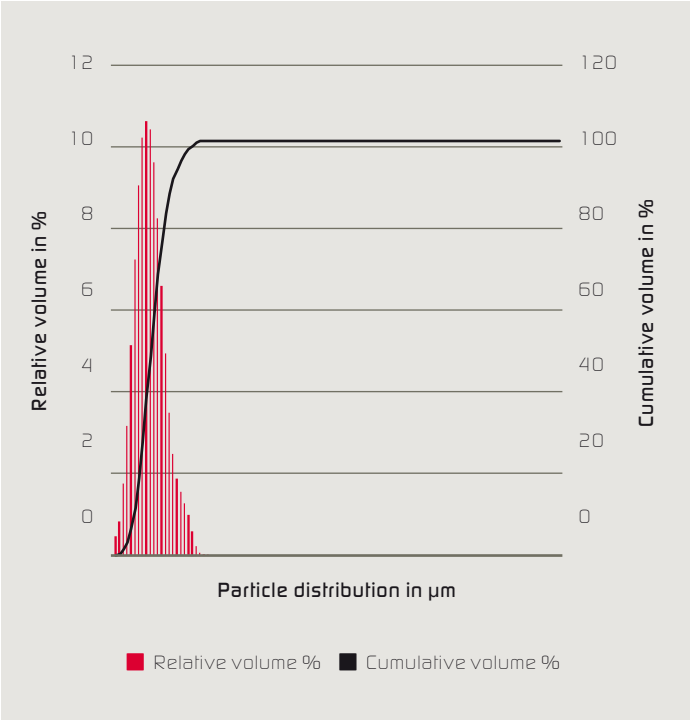
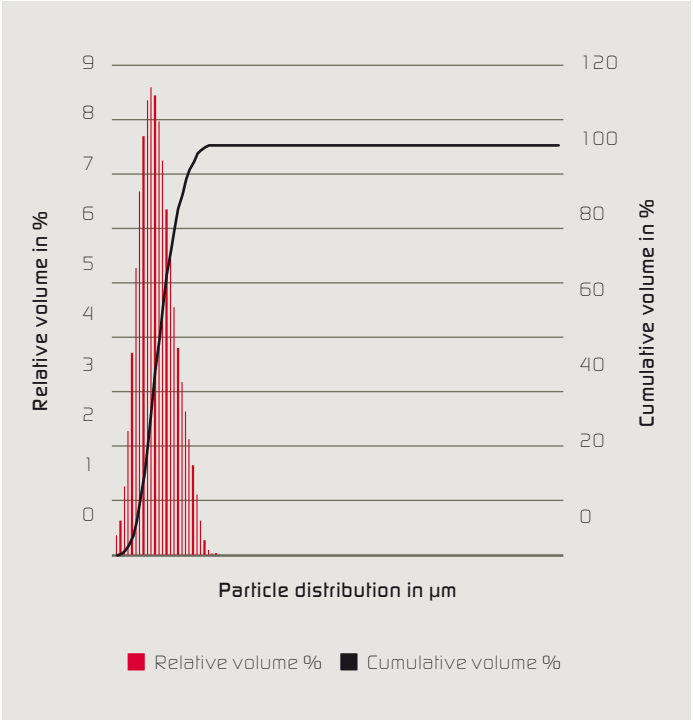


Figure 1b: Particle size distribution of the fumed silica slurry dispersions stabilised with DMEA.



RESULTS AT A GLANCE

→ Dispersions of fumed silica must be neutralised in order to maintain a stable form suitable for use in water-based coatings. Commonly used stabilisers such as dimethyl ethanolamine (DMEA) have a poor hazard profile and fail to meet the requirements of several eco-labels.

→ Dimethyl glucamine has been developed as a largely bio-based alternative with up to 75% renewable content which is completely safe (it is approved for use in unlimited amounts under various eco-labels).

→ A study of rheology curves for two different coating formulations thickened with fumed silica showed that the new stabiliser performs at least as well as DMEA. In some cases, better stability and efficiency were obtained when using dimethyl glucamine.

Usually, amine neutralising agents such as the aminoalcohol dimethyl aminethanol (DMEA) are used for this purpose. Due to its hazardous substance labelling and VOC content, this neutralising agent has limitations when used in a modern and environmentally conscious formulation.

A NEUTRALISER THAT MEETS ALL ECOLABEL REQUIREMENTS

Based on the general need for sustainable neutralising agents [6], Clariant has developed a sugar-based speciality amine that is new to the market [7]. The product is a dimethyl glucamine marketed under the name "Genamin Gluco 50".

The potential now available to improve environmental profiles following the introduction of this new sugar-based neutralising amine for the neutralisation and stabilisation of fumed silica dispersions is considered below. Its application and performance profile is discussed in detail in comparison to common neutralising agents on the market.

In order to create a comprehensive assessment of these neutralising agents, environmental, health and safety aspects have been considered in addition to performance characteristics. To support performance evaluation, comparative tests are based on fumed silica slurries of the "Aerosil" types developed by Evonik.

Matters such as labelling or VOCs play an important role, especially in relation to eco-labels. It is no easy task for a paint formulator to develop a high-quality paint that fulfils stringent ecolabel criteria.

Dimethyl ethanolamine (DMEA), however, is not suitable for paints and varnishes with the German Blue Angel RAL UZ12a, Nordic Swan for indoor paints and varnishes or the French Décret NF Environment because of its VOC content and its hazardous labelling, especially the hazard phrase H331 (toxic if inhaled).

In the evaluation of neutralising agents' suitability for ecolabels, dimethyl glucamine stands out as a multifunctional neutralising agent as it is the only one that can be used in unlimited amounts in paints which are certified according to the German Blue Angel, Nordic Swan or French Décret NF Environment. This is because the additive has no hazardous labelling and is VOC/SVOC-free.

Although the renewable content is not yet a criterion for ecolabels, another advantage of dimethyl glucamine is that it consists of up to 75% glucose and is therefore very much in line with the trend of renewable raw materials.
A selection of important sustainability aspects comparing dimethylglucamine to DMEA is listed in *Table 1*.

HOW NEUTRALISING AGENT PERFORMANCE WAS EVALUATED

In addition to the environmental, health and safety aspects, the performance of both neutralising agents was also evaluated. The neutralising amines were first formulated into fumed silica slurry dispersions and then 10% of these dispersions were incorporated into a PU-acrylic as well as into a styrene-acrylic clear coat.
The formulations were tested on the following criteria:

› Particle size distribution
› Flow curves
› Shear recovery

Dispersions were produced using an "Ultra Turrax" (UTE) dissolver, Skandex shaker or a Hilscher ultrasonic disperser. The starting formulations for the fumed silica slurry dispersions are described in *Table 2*.

INITIAL FLOW CURVE EVALUATION SUMMARISED

In *Figures 1a* and *1b*, the results for the particle size distribution of the fumed silica slurry formulations are shown after dispersing the fumed silica with the UTE disperser (circumferential or peripheral speed 13 m/s).
The particle size distribution of the dispersions with DMEA and dimethylglucamine show equivalent behaviour. This means that the dispersing and wetting time of both formulations are comparable and a switch from one neutralising system to the other would not affect the overall processing time.
Based on these results, flow curves of the fumed silica slurry dispersions were measured. When comparing the flow curves in *Figure 2*, dispersions prepared with the UTE disperser show slightly higher vis-

Table 1: Overview of the sustainability profiles of dimethylglucamine versus DMEA.

Neutralising agent	GHS labelling	Hazard statements	Flash point	VOC*	SVOC*	Biodegradation
Dimethylethanolamine (DMEA)		H226 Flammable H312 Harmful on contact with skin H331 Toxic if inhaled H302 Harmful if swallowed H335 May cause respiratory irritation H314 Causes severe skin burns and eye damage H402 Harmful to aquatic life	39 °C	Yes	No	Readily biodegradable
Dimethyl glucamine	none	none	> 100 °C	No	No	Readily biodegradable

* according to ISO 11890-2 and ISO 16000-9

Figure 2: Flow curves of the fumed silica slurry dispersions.

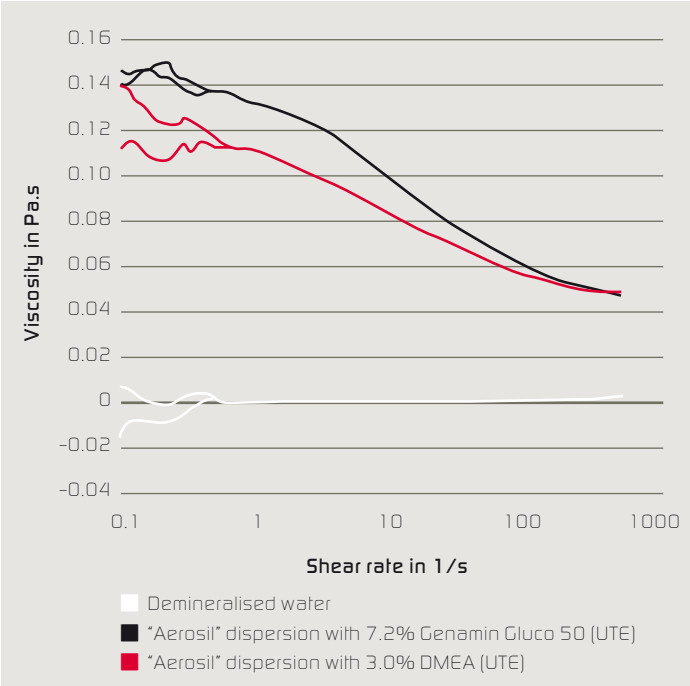
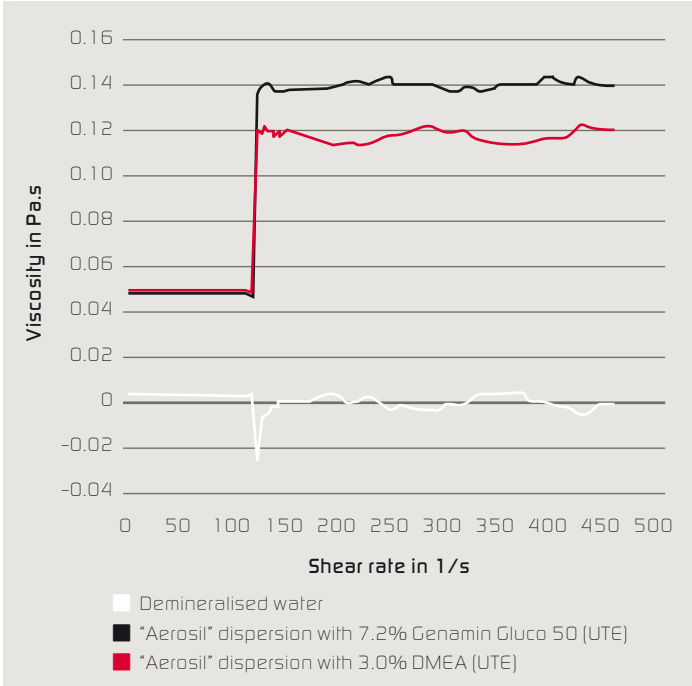


Figure 3: Shear recovery of the fumed silica slurry dispersions.



cosity for dimethylglucamine compared to DMEA. One advantage of a higher viscosity can be that less rheology modifier is required in the paint formulation in which the fumed silica slurry dispersion is used.

If the fumed silica slurry dispersions are required to have comparable flow curves and viscosity profiles over the complete shear range, additional dispersion using the Hilscher ultrasonic disperser is recommended. All dispersions tested were then water-thin.

In the next test, the dispersions were evaluated in relation to their shear recovery after high shear treatment. Dispersions with both stabilising agents had similar low shear thickening behaviour as shown in *Figure 3*. Under dispersion with the Hilscher ultrasonic disperser, an almost perfect Newtonian rheology was achieved.

This means that the levelling behaviour of both fumed silica slurry dispersions remains constantly at the same level. This is of particular interest as dimethylglucamine is a renewable-based additive and renewable ingredients are often considered by the industry to perform less well than non-renewable alternatives. The advantage of the constant levelling behaviour is that there is no need to change the paint recipe and/or use other additives to adjust the levelling behaviour.

RHEOLOGY CONTROL EVALUATED IN CLEAR COATS

10% of the fumed silica slurry dispersions were next formulated into clear coats. The main function of the dispersion in this application is rheology control. For this purpose, two water-based clear coat formulations based on the following binders were used:

- PU-acrylic hybrid dispersion: Solids content 35%; neutralisation: triethanolamine (TEA); pH value: 8.0.
- Styrene-acrylic copolymer: Solids content: 40%; neutralisation: ammonia; pH value: 9.0.

As can be seen in *Figure 4*, the PU-acrylic clear coat containing the fumed silica slurry dispersion which has been neutralised with DMEA shows a more pronounced rheology response, with a change of the viscosity behaviour during storage at room temperature between 24 hours and 28 days.

The analogous clear coat based on the fumed silica slurry dispersion with dimethylglucamine shows a very good, unchanged viscosity profile behaviour during the complete storage time, indicating improved wetting behavior with dimethylglucamine.

Dimethylglucamine shows excellent shear thinning behaviour and also good storage stability at low shear rates in comparison to the DMEA system. This means that the levelling behaviour of the PU-acrylic coating is excellent. Also, the absence of any significant change in the rheology behaviour between 24 hours and 28 days is especially valuable for the quality department of the paint manufacturer, as it is possible to test and evaluate the paint quality very shortly after its production. This helps to save valuable time and internal storage costs.
As can be seen in *Figure 5*, the styrene-acrylic clear coat containing the fumed silica slurry dispersion which has been neutralised with dimethylglucamine shows a more pronounced rheology response, with a higher viscosity at low shear rates compared to the corresponding formulation with DMEA. Achieving higher viscosities would allow the amount of fumed silica slurry dispersions and/or the rheology modifier in the clear coat formulation to be reduced.

HIGH PERFORMANCE IS COMBINED WITH A GOOD ECO-PROFILE

The most important applications of fumed silica slurry are rheology control, thickening, thixotropy, anti-settling of pigments and fillers and anti-sagging of coatings on vertical substrates.
Neutralising agents are only used in small quantities in water-based formulations. However, their effect is of significant importance in paints and in fumed silica slurry dispersions. Neutralising agents not only regulate the pH value, but also influence the dispersibility and storage stability as well as the rheology behaviour of the formulation. Dimethylglucamine is new to the market and was developed specifically for use as a multifunctional perfomance additive in ecologically-compatible, water-based paints. It contains up to 75% renewable raw materials, does not require labeling, is VOC/SVOC free and is there-

Figure 4: Rheology curves of the aqueous PU-acrylic clear coat.

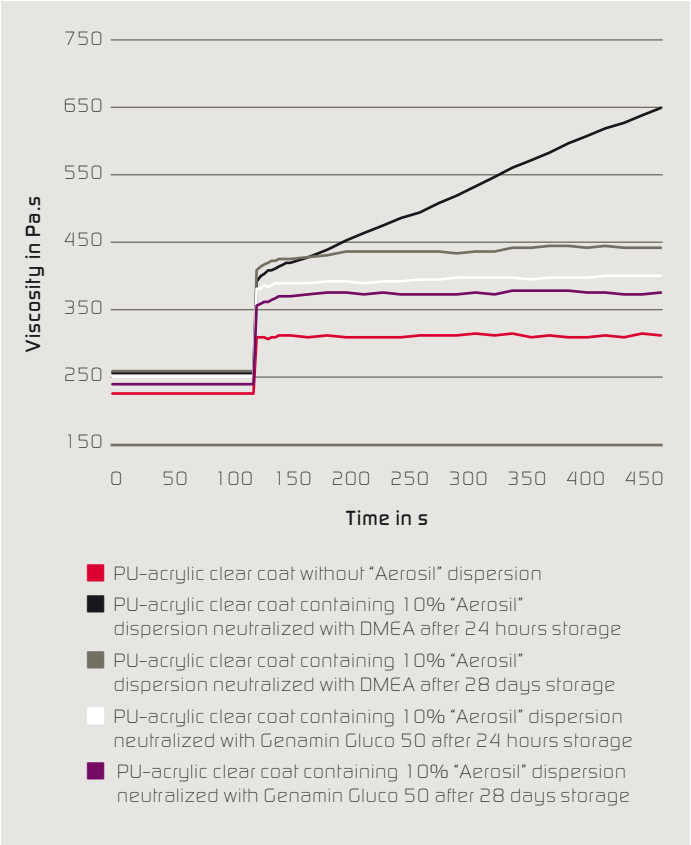


Figure 5: Rheology curves of of the aqueous styrene-acrylic clear coat.

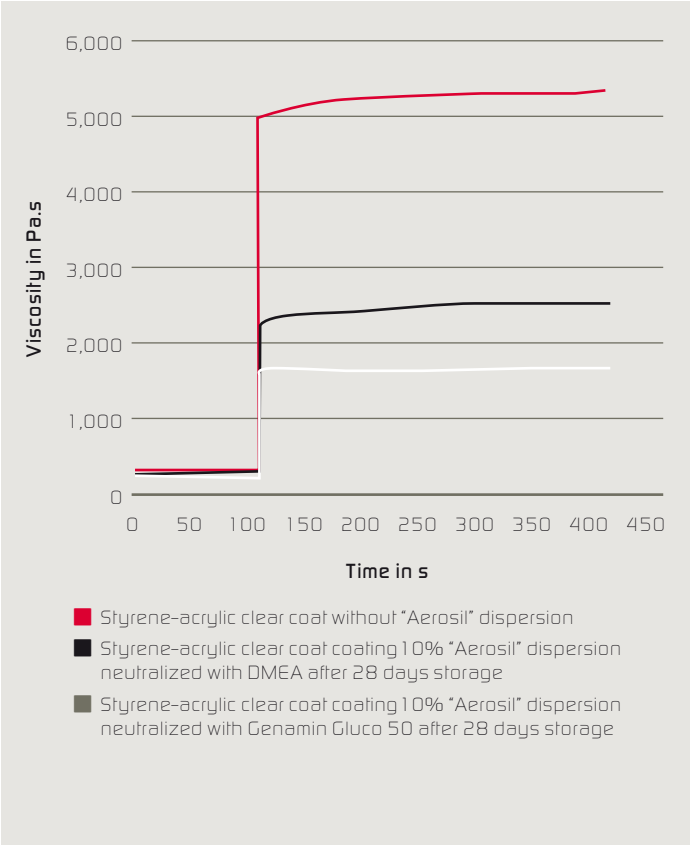


Table 2: Fumed silica slurry formulations with dimethylglucamine versus DMEA.

Ingredient	Fumed silica slurry formulation with dimethylglucamine (active content 50%)	Formulation with dimethylethanolamine (active content 98%)
"Aerosil" R 972	20%	20%
Wetting agent	10-20%	10-20%
Neutralising agent	4-8%	2-4%
Cosolvent	1-4%	1-4%
Defoamer	1%	1%
Demineralised water	Add up to 100%	Add up to 100%

"Formulators have the opportunity to reduce the levels of high-cost raw materials."

Jörg Rüger
Clariant Germany
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3 questions to Jörg Rüger

You repeatably claim that your additive is multi-functional. Which other functionalities beside neutralising does the new additive have? *Dimethylglucamine has a functionality as neutralising agent, stabiliser, wetting agent and rheology enhancer. The additive is not only used to adjust the pH-value of the fumed silica dispersion from a value of 10.0 to 10.5, but also to improve its storage stability, by avoiding syneresis or sedimentation and by maintaining a stable viscosity and pH-value of the formulation during long-term storage. This can be explained by the product's improved wetting behavior on the other ingredients of the slurry. Dimethylglucamine is also beneficial in influencing the rheology behavior of paints when prior used in the fumed silica dispersion. It increases the viscosity of the paint formulation and in consequence less amount of rheology modifier is required.*

Your tests with the acrylic test system indicated an improved wetting behavior of the dimethylglucamine. Did you saw similar results for the styrene-acrlic copolymer system? *We saw different results from different systems. In the styrene-acrylic clear coat system, we observed the same initial rheology curve as the acrylic system. After 28 days, we observed an increase in the viscosity of the styrene-acrylic system that did not occur in the acrylic system. Due to the increase in viscosity over time of the styrene-acrylic system, formulators have the opportunity to reduce the levels of high-cost raw materials in styrene-acrylic formulations, including rheology modifiers or the amount of fumed silica slurry.*

What is the source of your bio-based content. Is it in competition to the food supply chain? *Dimethylglucamine is based on glucose, extracted from European non-gene-modified corn. The product's renewable content is 75% according to the renewable carbon index RCI. (Dimethylglucamine consists of 8 carbon atoms, thereof 6 atoms are sugar-based. The other 2 are of synthetic origin.) As glucose can be used in the food production, there is a certain competition with the food supply chain. But in comparison to other raw materials such as palm oil where there is a valid discussion ongoing on how to improve the impact on people and planet, sugar or glucose is abundantly available on the world market. We therefore did not consider this aspect as a major risk in the sustainability assessment of our product. Dimethylglucamine underwent a thorough screening against 36 criteria covering the entire product lifecycle and was also benchmarked against market standards. Due to the product's outstanding sustainability profile, dimethylglucamine has therefore been awarded Clariant's EcoTain label.*

fore especially suitable for eco-label certified lacquers and varnishes. From a performance point of view, this is a multifunctional additive that allows stable, pumpable and label-free fumed silica dispersions to be produced. In addition, clear coat formulations containing fumed silica slurry dispersions that have been previously neutralised with dimethylglucamine show excellent rheology performance. This offers the possibility of improving the cost/performance of the paint as the overall amount of fumed silica slurry dispersion can be adjusted in the formulation.

The ingredient combines multi-functionality with an excellent eco-profile and is therefore a new, highly valuable ingredient for the paints and coatings industry as it seeks to address increasing requirements from end-users and the industry's own priorities.

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