WHITE PAPER

LEVERAGING SURFACTANT STRUCTURE-PROPERTY RELATIONSHIPS TO ADDRESS EMERGING NEEDS IN COATINGS

Christine Louis, K. Michael Peck

EVONIK
Leading Beyond Chemistry

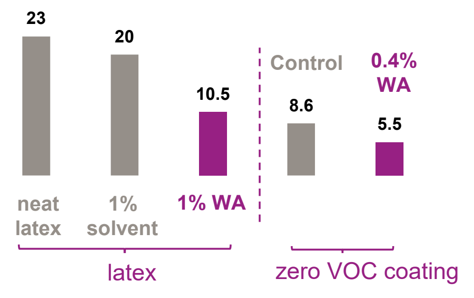
ABSTRACT

All surfactants are amphiphilic molecules that orient at interfaces; however, a surfactant's exact chemical structure will dictate its behavior at these interfaces. In dilute systems, this is well understood, but in the complex formulation of most coatings applications the behavior becomes far more difficult to predict. The guidelines originally developed for commodity surfactants in dilute detergent systems translate poorly to coatings, requiring greater understanding of surfactant structures as well as their interactions with other components. These interactions can significantly alter a surfactant's behavior, causing loss of efficiency, unanticipated effects in the finished coatings, and hurdles for the chemist in optimisation of the formulation. This paper will discuss some of these effects and review recent surfactant structure-property relationship studies in pigmented systems that provide insight into how the variation of specific chemical structural features modifies the resulting surfactants' interactions with other coatings components. Additionally, the combination of these structural elements to create next generation wetting agents will be described.

INTRODUCTION

Surfactants are commonplace in aqueous coating formulations and are added to achieve a variety of performance effects. Substrate wetting, dispersancy, emulsification, and color acceptance are some of the most common attributes, but surfactants are impactful in a number of other areas. With ongoing formulation changes being made to meet ever more stringent environmental, health, and safety considerations, the impact of surfactants has become increasingly important and, too often, sub-optimal product selection leads to negative formulation impacts, overdosing, and greater rework. Much of current surfactant formulation understanding is rooted in older theories like HLB[1,2] (Hydrophilic - Lipophilic Balance) that are limited in complex systems like coatings. Newer theories and approaches are required to both develop optimized products and reduce formulation time. A greater understanding of surfactant partitioning in a complex formulation is a vital tool to drive innovation and this has been used to good effect in many areas. Wetting agents can be tailored in chemistry and function to orient at a latex particle even within a complex coating and provide benefit in film coalescence and minimum film formation temperature reduction. This performance can offer options to reduce solvent, optimise formulation, or achieve differentiated coating behaviors. Chart 1 below highlights the impact of this type of surfactant in a styrene-acrylic latex as well as its use in a zero-VOC formulated paint based on this latex.

Chart 1. Impact of a wetting agent on Minimum Film Formation Temperature (°C)



On the left of Chart 1 are the MFFT (minimum film formation temperature, evaluated in a manner similar to ASTM D2354-10) results in the styrene-acrylic latex, with the neat latex showing a MFFT of 23 °C while 1 wt% of the recommended co-solvent reducing the MFFT to 20 °C. The use of a coalescing surfactant at the same level provides a noticeably lower MFFT of 10.5 °C. On the right side of Chart 1, the results in a fully formulated semi-gloss paint are shown for the resin supplier's recommended model formulation and the same formulation containing 0.4 wt% of a coalescing surfactant, with MFFT values of 8.6 °C and 5.5 °C, respectively. The impact on MFFT at low levels of coalescing surfactant is significant and provides an additional benefit on top of an outstanding wetting performance contribution. This effect provides opportunity for a formulator to optimise for lower solvent usage or further MFFT reduction as performance needs dictate.

Chart 2. Impact of an open time extending surfactant on working time (min)

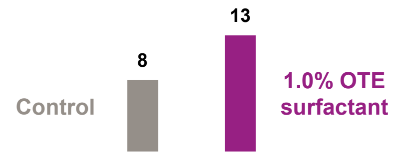


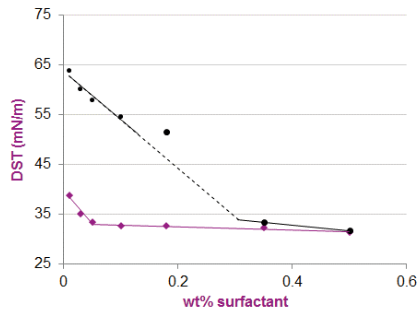
Chart 2 below shows the results for a different surfactant that was designed to impact open time in low and zero-VOC aqueous coatings. The open time of a formulated wall paint as measured by ASTM D7488-11 is shown for a commercial paint both without and with the use of a surfactant designed to extend workability and open time. At a 1 wt% use level, the paint sample shows significant increase in open time and offers potential for a formulator to meet market needs.

These performance attributes rely on the partitioning of the surfactant between continuous phase, particle surface, and other interfaces within the complex paint formulation. Optimising this behavior is a key attribute in maximising the desired performance while minimising secondary effects on the final product. These examples highlight just two current approaches in surfactant technology that add differentiated value to a formulator. More effects are possible with a greater understanding of component interactions and one of the more challenging and technically fascinating areas is the orientation of surfactants in pigmented systems and the interaction with dispersants and resins. Work in this area will be discussed in this paper and details of the experimental approach leading to an optimised surfactant suitable for colorants and pigmented coatings will be described.

INTERFACIAL ACTIVITY IN COMPLEX SYSTEMS

It is typical to see surfactant performance quantified and described in pure water. Equilibrium and dynamic surface tension (DST) measurements and foam stabilisation assessments are useful to understand fundamental characteristics, but behavior in pure water can be very different than even the simplest formulations. The addition of other components can radically alter a surfactant's behavior. Chart 3 below demonstrates this in a comparison of the surface tension reduction ability of a commodity ethoxylated alcohol surfactant in pure water (purple) and the same surfactant in the presence of a very small amount of an organic pigment (black).

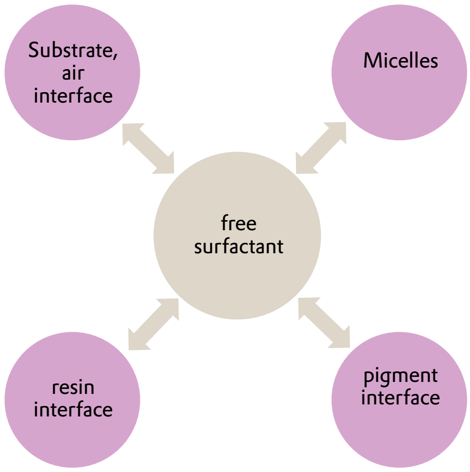
Chart 3. Surface tension reduction in the presence of pigment red 22



Measured in pure water, this surfactant exhibits a minimum dynamic surface tension at approximately a 0.05 wt% surfactant addition at the CMC (critical micellization concentration) as measured at 0.1 b/s using a bubble tensiometer. In the presence of 2 % pigment, the dynamic surface tension reduction is noticeably reduced, indicating a clear and significant loss of surfactant to the pigment-water interface. With the addition of the pigment, the surfactant in the system is now depleted from the continuous phase, lowering the available surfactant concentration for surface tension reduction at the gas-liquid interface. Minimum surface tension reduction is not achieved until at least a five-fold increase of the surfactant loading. The new CMC is extrapolated to a 0.3 wt% concentration although the data set is not large enough to fully elucidate the behavior. It is possible that the extrapolated curve is non-linear with a secondary plateau present due to the adsorption at the solid-liquid interface.[3]

Adsorption behavior may be preferred for a surfactant chosen for use as a pigment co-stabiliser, but it would certainly be undesirable for a surfactant used for wetting of a substrate. In a fully formulated coating, the situation becomes even more complex with multiple interfaces and large surface areas serving to deplete any surface active additive used in the system. Figure 1 below describes this in a simplified schematic. Surfactants within a formulation will be distributed among all the available phases and interfaces within a complex system.

Figure 1. Surfactant location in a complex formulation

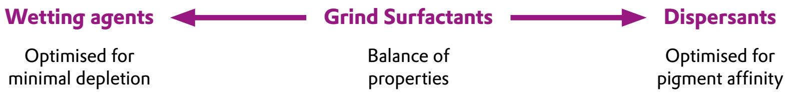


A full understanding of the location of each surface active material in a formulation would be ideal but the complexity of the system makes direct analysis difficult. For the present, a piecemeal investigation can provide insight and guide product development.

SURFACTANTS IN PIGMENTED SYSTEMS

In a pigmented system, it is common to see multiple surface active materials used. Dispersants, grind resins, or binders are employed to stabilise against flocculation and wetting agents are often used to improve wetting of both substrate and dry pigment. It is also typical to see alkoxylated surfactants utilised for a mix of stabilisation and surface tension reduction, impacting a wide range of formulation attributes. This latter category is of interest because the behavior of these products is likely the least understood and the most prone to misuse, overdosing, and unanticipated side effects. Figure 2 below describes the general attributes of these product groups.

Figure 2. Surfactants in a pigmented system



On the left most side, wetting agents provide optimal surface tension reduction for both process and application to a substrate. Products are optimised by maximising the available surfactant concentration in the continuous phase and availability for orientation and energy reduction of any new interface such as a substrate. On the right side, dispersants are optimised for stabilisation of the pigments or other solids against flocculation. They are tailored for strong interaction at the solid-liquid interface. The stabilising surfactant however is typically utilised for multiple properties. Alkylphenol ethoxylates, alcohol ethoxylates and specialty chemistries are used for improved milling and color development, steric stabilisation benefits, color acceptance, as process aids, as well as for cost effective wetting benefits, but side effects are common particularly due to poor product selection and overdosing. Rheology impacts, water sensitivity, leaching, reduced stain resistance and foam are common results. Optimisation of the product and use ideally leads to minimal loading levels reducing formulation costs and minimises negative effects that reduce coating performance. The ideal grind surfactant then, would provide optimal process and performance impact at the lowest use level with no negative side effects.

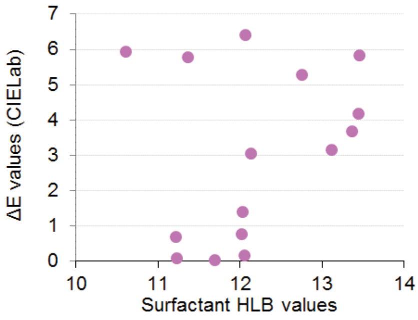
INTERFACIAL ACTIVITY

Grind surfactants appear to require a balance of properties for optimal performance. Surface tension reduction is a known requirement of pigment milling.[4] Adequate interfacial tension reduction ensures complete wetting of the pigment and reduces the energy required to mill the pigment. This is certainly a key component, but, if surface tension control were the only driver, it would be expected that formulators of dispersions would primarily use wetting agents. This is not the case, however, and alkoxylated surfactants appear to play a more common role than wetting agents alone.

It is also expected that steric stabilisation is an important factor in the milling, compatibilisation and stability of the finished product. This has been discussed widely in the literature,[5] but what is less clear is the optimal combination of these two properties in a complex coating formulation. The common use of multiple surfactants in coatings indicates that there is a necessary balance for optimal performance that it is often identified through trial and error testing. Elucidation of this balance is an important first step towards surfactant optimisation.

One of the more common surfactant selection criteria is the HLB of the surfactant. This is essentially a description of the relative size of the steric stabilisation component of the surfactant and is often used to guide product choice. HLB theory may have utility in dilute emulsions, but empirical data suggests its utility in coatings is limited. It is not uncommon to find a system served equally well by surfactants of widely disparate HLB values. A study into applicability of HLB in an organic orange pigment colorant is shown in Chart 4 below. This system is one where a replacement of an APE surfactant was needed and APE-free surfactants of similar HLB value to that of the incumbent product were chosen for evaluation. The surfactants evaluated all have an ethoxylated A-B structure but differ in the nature, shape, and size of the hydrophobe. No trend is apparent relative to HLB value and large differences are seen in the performance of surfactants of the same HLB value.

Chart 4. Surfactant HLB and color development



This data set suggests that single factors like HLB used to characterise a surfactant may be inadequate for broader product selection. Something more is at play and factors such as hydrophobe size, bonding interactions, structure, and stabilisation characteristics may be potential areas for investigation.

SURFACTANT PARTITIONING

To explore surfactant behavior in a complex system, an attempt was made to first determine the nature of surfactant pigment interaction. To accomplish this, dispersions were prepared based on various grind surfactants. Color development and stability were evaluated as critical performance criteria. Additionally, a centrifuge (10 k -25 k rpm) was used to force separation of pigment from the liquid to allow a direct quantification of surfactant partitioning between the pigment water interface and the continuous phase. The finished dispersions were diluted 1:1 with water prior to centrifugation to eliminate any rheology differences in the dispersions. It is expected that this would cause deviation from the true partitioning of the surfactant in the system, but it should permit a valid comparative analysis between different surfactant types. Additionally, it is expected that the dilution and centrifugation would be a net driver for increased surfactant content in the supernatant and that values remaining with the pigment a minimum relative amount.

A higher surface area untreated phthalocyanine pigment was used to increase the expected differentiation between surfactants and this was combined with a strong pigment affinic dispersant that was considered unlikely to stay in the continuous phase. Multiple evaluations prior to broad testing confirmed that no dispersant was present in the collection liquid phase and no other materials were present in significant amounts in the supernatant. Liquid chromatography was used for direct analysis of the surfactant content in the continuous phase and this was confirmed and expanded upon with mass balance measurements of the separated phases. FTIR (Fourier Transform Infra-red) was used to confirm general chemistries and as a spot-check to verify that other components were not separating. A ladder study of a common benchmark alcohol ethoxylate was initially evaluated (shown in Table 1 below) and provides some interesting insights.

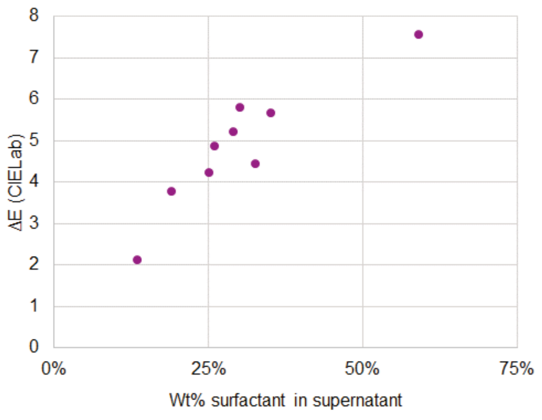
Table 1. Amount of surfactant present in supernatant related to surfactant concentration present in the dispersion

SURFACTANT USE LEVEL (*g* per 100 *g* dispersion)	SURFACTANT IN SUPERNATANT (*g*)
1	0.5
2	0.7
4	1

The majority of the benchmark surfactant appears to stay with the pigment, indicating that this surfactant would be better suited for pigment stabilisation and less available for utility at other interfaces or for a wetting function. Even at high use levels, the surfactant appears to deplete at the pigment interface and remain there, even after dilution and centrifugation.

Using the same approach, this technique was applied to a range of surfactant types to determine if differences are evident. Chart 5 below shows a compilation of results for different surfactants based on different hydrophobes, A-B and A-B-C structures, and alkoxylation levels. This evaluation was comparable to that described above and the surfactants are compared at a consistent 2 wt% use level. Ladder studies were conducted for selected samples and showed trends similar to the results shown in Table 1 previously.

Chart 5. Delta E values as function of surfactant amount present in the supernatant



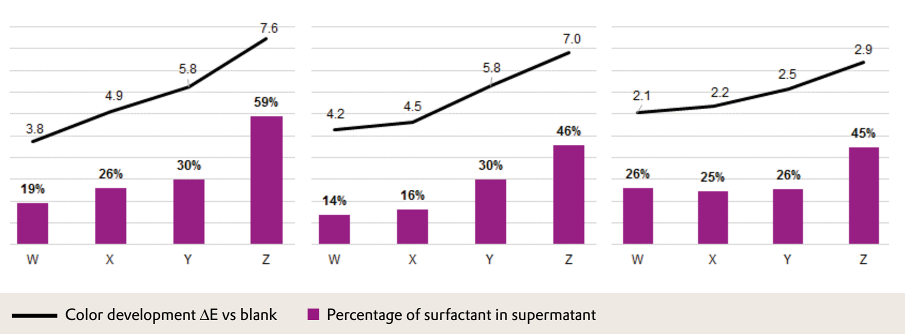
The surfactants shown in Charts 6, 7, and 8 are only those products that demonstrated suitable dispersion stability and rheology performance. Products that did not provide adequate stabilisation or resulted in poor dispersion rheology were excluded to avoid potentially misleading results.

The results in Chart 5 indicate a positive relationship between color development of this untreated phthalocyanine blue and surfactant content in the supernatant. The colour development was evaluated in drawdowns of a tinted white base paint and ΔE (CIELab) values were calculated relative to a control prepared with no grind surfactant. This performance may be related to surface tension reduction, but other factors related to the steric stabilisation contribution are expected as well. The surfactant content in the supernatant is well above CMC values for these surfactant types, measured to be around 0.02 to 0.1 wt%. The data point in the lower left of Chart 5 is the result of an A-B type surfactant with a strong hydrogen-bonding hydrophobe expected to have a greater affinity for the pigment surface. This gives further credence to the premise that the results are capturing differentiation between surfactant partitioning and not an artifact of another issue. As a next step, a selection of four of the surfactants that span the data range was made and the experiment was repeated with changes in dispersant and pigment chemistry. Chart 6 below replicates the results of Chart 5 for these four selected surfactants with the phthalocyanine pigment, showing the measured surfactant in the supernatant as the bar and color development results as the line. Chart 7 shows the results for the same surfactants with a change in dispersant from a styrene-acrylic to a polycarboxylate type. Chart 8 shows the results for the same surfactants with a change in pigment to an organic yellow, PY83. The trend of these four surfactants is consistent across the changes in formulation chemistry. All four provided stable dispersions of comparable rheology, but clearly showed differences in color development that appear to follow a trend of increasing 'free' surfactant content in the supernatant.

Chart 6.
Pigment 1, acrylic dispersant

Chart 7.
Pigment 2, polycarboxylate dispersant

Chart 8.
Pigment 2, acrylic dispersant



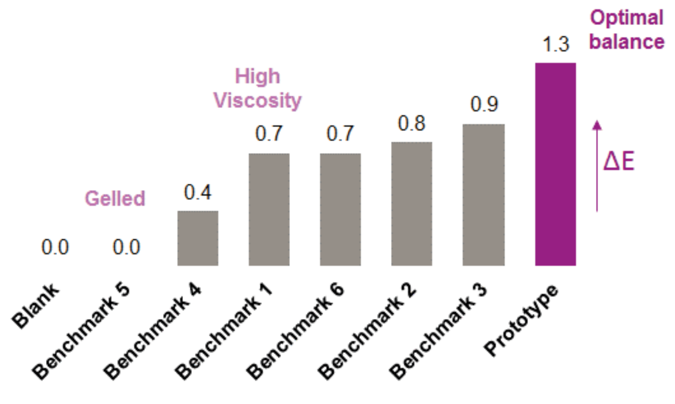
The results found in the free surfactant analysis support a premise that surfactant performance in a pigmented system is related to how the surfactant partitions between the pigment-liquid interface and the bulk continuous phase. They also suggest that the surfactant structure properties are a larger factor than the system chemistry. This is not counter to current theories and may hint at answers to open questions about why some surfactants are successful and others are not. A surfactant that offers an ideal balance between depleting to the pigment surface and providing a steric stabilisation benefit and remaining in the continuous phase to interact with new or changing surfaces and provide wetting benefit would be anticipated to offer the optimal efficiency.

Additionally, the suggestion that surfactant structure is more important than system chemistry is a great boon to additive designers. The ability to intelligently develop surfactant chemistry within a smaller scope of formulation impacts allows much greater flexibility in addressing regulatory hurdles. Product volatility and indoor air emissions can be addressed with higher molecular weights and lower amounts of byproducts or unreacted alcohols. Products can be developed to reduce or avoid environmental, health, and safety issues that create risks for the formulator or inhibit compliance with initiatives such as LEED or EcoLabel.[6]

PRODUCT DEVELOPMENT

Expanding on the experimental findings described above, an effort was initiated to develop a product that provided an optimal balance of performance, avoided EH&S, VOC, and emission impacts that would limit its viability in all types of waterborne coatings, particularly for indoor applications. The specifics of this work are not suitable to share due to the proprietary nature of the chemistry, but were focused on the depletion studies as described in this paper. Chart 9 below shows the culmination of this work with the performance of a prototype grind surfactant in a fully formulated zero-VOC coating based on pigment yellow 74 and a common high performance comb polymer dispersant. Increased color and stability improvements are noticeable over the benchmarks.

Chart 9. Prototype performance in a PY74 paste – ΔE increase compared to blank



Optimised performance results from identification and utilisation of the surfactant characteristics that provide an ideal balance of depletion and free surfactant. Similar trends are seen with different dispersions.

This performance also appears to translate to fully formulated coatings as well. The increased complexity inhibits clear differentiation between surfactants in one single property like color, but, instead, typically result in subtle variations and defects in coating performance. Hiding power, rheology, water sensitivity, blocking, and stain resistance are common areas where surfactants can drive noticeable and quantifiable changes in performance. Table 2 below shows the results of a prototype surfactant in a zero-VOC, interior, semi-gloss paint formulation based on a styrene-acrylic latex. This system was taken from a published model formulation that utilised a common alcohol ethoxylate surfactant in the grind.

Table 2. Paint performance properties using a prototype surfactant in a zero-VOC, interior, semi-gloss formulation

		Surfactant overdose		Optimal performance
	CONTROL	**WETTING AGENT ADDITION**	**PROTOTYPE REPLACING BOTH**	**PROTOTYPE, 50 % USE LEVEL**
WETTING/ DEFECTS	Poor	Excellent	Excellent	Excellent
BLOCKING (1-10, 10 best)	6	4	7	7
LEACHING, 4 DAY (1-10, 10 best)	8	6	8	8

The paint was prepared as specified and evaluated for typical coating performance properties. The control formulation showed evidence of wetting inefficiencies on various substrates as well as mild defoamer related defects. Extrapolating from the results discussed in this paper, it is likely that the alcohol ethoxylate was largely depleted from continuous phase of the formulation and unavailable for substrate wetting. The typical recommended solution for this is the addition of another surfactant, a wetting agent to improve performance. This was attempted, using a 0.1 wt% addition of a wetting agent with results shown in column 2. The wetting deficiency was resolved, but the small addition of surfactant resulted in a noticeable drop in blocking and only a slight improvement in the leaching performance. This can be attributed to a surfactant content that is partitioned to the wrong interfaces in the coating formulation, leading to a reduction in properties. A switch to the prototype surfactant at the same use level erases these deficiencies and improves upon both the wetting and blocking performance of the control model formulation. The efficiencies of the prototype surfactant allow further use level reduction, maintaining performance even with 50 % less loading. Proper surfactant location in the complex system allows optimal performance at a minimal use level.

PRODUCT DEVELOPMENT

The investigation and product development discussed in this paper demonstrate that surfactant performance can vary significant in formulated systems. There are strong indications that the variation is related to the partitioning of a surfactant to the different interfaces in a formulation and is attributable to the surfactant chemistry itself. A number of products are tailored for activity at select interfaces, whether co-dispersants for the pigment surface or coalescing surfactants to the latex particle. This approach to optimisation can be applied to general surfactants as well and is particularly effective in aqueous pigmented formulations. A surfactant with the appropriate balance of properties can provide both the stabilization performance necessary for color acceptance, dispersion stability, and compatibilisation, while maintaining adequate free surfactant content available for wetting, milling, and process requirements. This balance allows the formulator to use a minimal surfactant loading, reducing the risk of performance deficiencies such as foaming, blocking problems, leaching and water resistance or rheology problems typically associated with surfactant overdosing.

Optimally performing surfactants that meet current and future regulatory hurdles are a key step in continuing to drive innovation and performance improvements in coating technology.

ACKNOWLEDGEMENT

The authors would like to acknowledge the work and contributions of Timothy Smith, Michael Pauley, Renae Bennett, Jonathan Sefko, and Wilco Chaigneau to the research, analysis, and product development discussed in this paper.

REFERENCES

1) Griffin, William C. (1949), Classification of Surface-Active Agents by 'HLB', Journal of the Society of Cosmetic Chemists, **1** (5): 311-26
2) Davies JT (1957), A quantitative kinetic theory of emulsion type, I. Physical chemistry of the emulsifying agent, Gas/Liquid and Liquid/Liquid Interface, Proceedings of the International Congress of Surface Activity, pp. 426–38
3) Johnsson, Bo, et al (1998), Surfactants and Polymers in Aqueous Solution, John Wiley & Sons, pp 219–220
4) Winkler, Jochen (2012), Dispersing Pigments and Fillers, pp 59-96
5) Tadros, Tharwat F. (2005), Applied Surfactants: Principles and Applications, chapters 5, 6, 7
6) www.ecolabel.eu

AUTHORS

K. Michael Peck, Evonik Corporation, USA
Christine Louis, Evonik Materials Netherlands BV, The Netherlands

Evonik Operations GmbH
Goldschmidtstraße 100
45127 Essen
Germany
Phone +49 201 173-2222
Fax +49 201 173-1939
coating-additives@evonik.com

ACEMATT®, ADDID®, AEROSIL®, AIRASE®, ALBIDUR®, CARBOWET®, DYNOL™, NANOCRYL®, SILIKOFTAL®, SILIKOPHEN®, SILIKOPON®, SILIKOPUR®, SILIKOTOP®, SIPERNAT®, SURFYNOL®, TEGO®, TEGOMER® and ZETASPERSE® are registered trademarks of Evonik Industries or its subsidiaries.

Evonik supports you in selecting the best suited product and optimizing current formulations through our Application Technology Group.

2020_12

EVONIK
Leading Beyond Chemistry