

实现水性涂料更好润湿的不同方法

Different Approaches to Achieve a Better Wetting of Waterborne Coatings



涂料是一个多组分系统，表面 / 界面对其质量有很大影响。表面缺陷经常在涂料应用期间和之后发生，并且会降低涂层的光学性能及对基材的保护能力。最常见的缺陷是基材润湿性差、流动性不佳（橘皮）和形成凹坑。

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影响所有这些缺陷的一个非常重要的参数是相关材料的表面张力。更具体地说，表面张力差异是这些表面缺陷的实际原因。表面张力差异的来源可能来源于系统本身（溶剂蒸发或树脂的交联反应）或来源于外部（过喷、灰尘颗粒或基材污染）。

现代水性涂料面临许多技术和商业挑战。涂料添加剂已成功用作涂料配方中的「问题解决者」，并且在水性涂料配方设计师满足不断增长需求并推动技术进步方面变得越来越重要。

润湿现象是关键点之一，特别是在水性涂料中，因为其表面张力较高。因此，使用合适的润湿剂变得至关重要。向涂层 / 空气或涂层 / 基材界面迁移并调整表面或界面张力的添加剂可以改善润湿性。本文中，我们将讨论降低待涂涂层表面张力的常规途径，以及通过亲水性添加剂增加底层涂层表面能的第二种途径，这对后续涂层的润湿有积极影响。与可重涂性有关的各种未解决问题是开发第二个独特机会以构建多层系统的驱动因素和动机。我们最近开发的亲水性添加剂是多功能的，将滑爽性与亲水性相结合，是一种独特的效果组合。

Coatings are multi-component systems and surfaces/ interfaces have a strong influence on their quality. Surface defects often occur during and after coating application, and degrade both the optical properties of the coating and its ability to protect the substrate. Most common defects are poor substrate wetting, non-optimal flow (orange peel) and crater formation. One very significant parameter affecting all these defects is the surface tension of the involved materials. More specifically, surface tension differences are the actual cause of these surface defects. The source of surface tension differences can be within the system itself (solvent evaporation or the crosslinking reaction of the resin) or external sources (overspray, dust particles, or contamination of the substrate).

Modern waterborne coatings face a number of technical and commercial challenges. Coating additives have been used successfully as "problem solvers" in coating formulations and are becoming of increasing importance to enable waterborne coatings formulator to reach the ever increasing demands and to advance the technology.

The wetting phenomenon is one of the crucial point, especially in the waterborne coatings as their surface tension is higher. Consequently, using the appropriate wetting agent becomes of upmost importance. Additives that migrate toward the coating/air or coating/substrate interface and tailor surface or interface tension can improve the wetting.

引言：实现更好润湿的各种方法

改善基材润湿性的经典方法是使用添加剂，以降低涂料自身的表面张力。氟化表面活性剂和有机硅表面活性剂是这组添加剂中最有效的物质。即使少量，它们也会降低涂层的表面张力并有利于铺展。多年来，涂料配方师主要使用这种工具来改善基材润湿性，但也用于改善涂料在底漆、中涂漆层上的润湿性。这仍然是提高固化涂膜润湿性的第一种方法，但该方法在多层涂装体系存在许多缺点。首先，涂层的低表面张力对于实现最佳流平来说并不理想。其次，必须考虑涂层之间以及与基材之间的润湿过程。如果底层具有相对较低的表面能，则在多层涂层中添加调节表面张力可能会出现严重的问题。最后需要注意的是，许多润湿添加剂可能会导致严重的泡沫稳定问题，尤其是在使用氟化表面活性剂时。

在大多数涂料配方中，使用有机改性聚硅氧烷（经典有机硅添加剂）降低表面张力，例如，以聚硅氧烷作为主链，聚醚作为端链或者侧链的有机硅添加剂。有机硅添加剂可改善对基材或者底层涂层的润湿性，并提高抗缩孔性能。然而，活性更高的有机硅添加剂同时会降低固化涂层的表面能。

多层涂层系统的一个新的独特机会不是使用基材润湿添加剂，而是提高底层涂层（或底漆）的表面能，这样后续涂层就不需要传统的润湿添加剂。首次开发出新一代亲水性添加剂，与其它表面添加剂不同，它能够显著提高固化涂膜的表面能。这导致后续涂层的完美润湿和重涂时良好的层间附着力。

结果与讨论：化学和应用结果

流平添加剂是许多涂料体系的重要组成部分，它们通过在干燥和固化过程中最大限度地减少表面张力的差异来发挥重要作用，从而产生光滑的表面外观。

第一代流平添加剂是标准丙烯酸烷基酯或甲基丙烯酸

In this paper we will discuss both the conventional route to decrease the surface tension of the coating to be applied, and a second route to increase the surface energy of an underlying coating by hydrophilic additives, which positively affects the wetting of the subsequent coating layer. Various unresolved issues with recoatability were the drivers and motivation for developing this second and unique opportunity to build up multi-layer systems. The hydrophilic additives we recently developed are multi-functional and combine slip to the hydrophilic properties, a unique combination of effects.

Introduction: various ways of achieving better wetting

The classic approach to improving substrate wetting is to use an additive, which reduces the surface tension of the coating to be applied. Fluorinated surfactants and silicone surfactants are the most effective substances in this group of additives. Even in small quantities, they reduce the surface tension of the coating and favour the spreading. For many years, coating formulators used primarily this tool to improve the substrate wetting but also the wetting over primers, basecoats, middle coats etc. This is still the first approach to improving the wetting of cured coating films, but the method has many disadvantages in multi-layer coatings. Firstly, a low surface tension of the coatings is not ideal for achieving the best possible levelling. Secondly, it is necessary to consider the wetting process of the different layers between each other and with a given substrate. The adjustment of the surface tension with additives in multilayer coatings can be problematic if the underlying layers have relatively low surface energies. Last but not least, many of the wetting additives may cause a serious foam stabilisation issue especially when using fluorinated surfactants.

In most coating formulations, the surface tension is reduced using organically modified polysiloxanes (classical silicone additives), in which for example, the polysiloxane forms the backbone and the polyether the end or side chains.

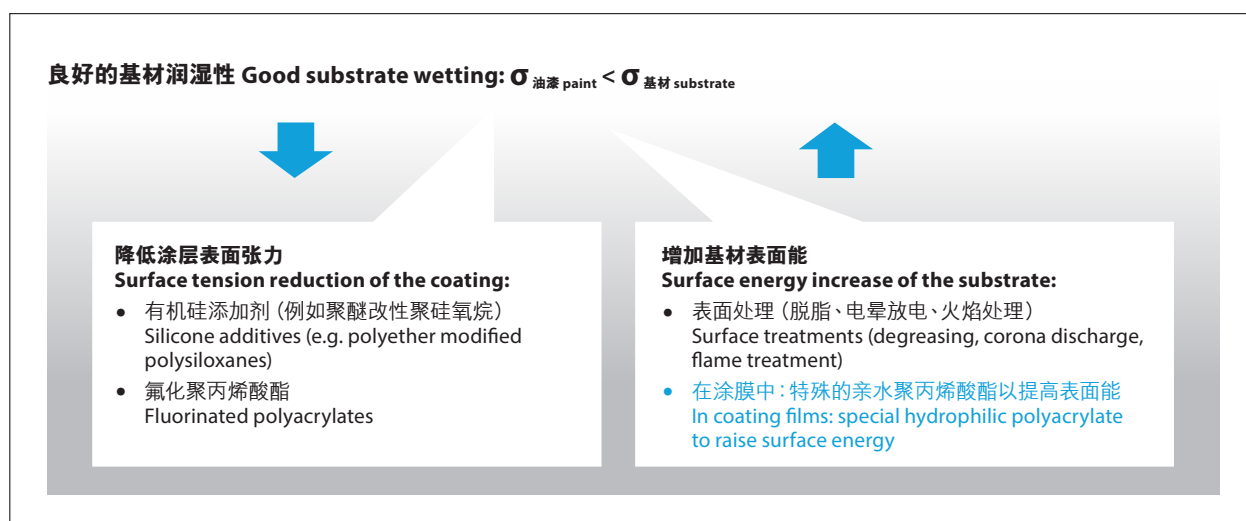


图1：有机硅添加剂可改善基材或底层涂层（底漆）的润湿性并增强抗缩孔性能。

Figure 1: Silicone additives improve the wetting of substrates or of the underlying coatings (primers) and enhance the anti-crater performance.

烷基酯的均聚物或共聚物。(甲基)丙烯酸酯单体是含有可聚合双键的小分子,该双键与其它单体共价结合以构建聚合物链。(共)聚合物链的结构是线性的。基于聚丙烯酸酯的流平添加剂与涂料基体略有不相容。因此,聚合物链迁移至涂层表面,并在固化过程中保持表面张力恒定。通过选择合适的单体和聚合条件,可以广泛地改变助剂的化学结构和极性。设置聚合度 n 来决定分子量的大小,通过改变 R^2 基团来控制极性(图 2a)。几十年来,第一代结构 1 流平添加剂(表 1)一直是最先进的。

下一代流平添加剂的开发通过影响液体/固化涂料的表面张力/能量提供了额外的好处。这些梳形共聚物结构在技术上可通过使用特殊的功能化组分,即所谓的「大分子

Silicone additives improve the wetting of substrates or of the underlying coatings (primers) and enhance the anti-crater performance. At the same time however, the more active silicone additives, in particular, reduce the surface energy of cured coatings.

A new and unique opportunity for multi-layer coating systems is not to use a substrate wetting additive, but to raise the surface energy of the underlying coating (or primer), so that no conventional wetting additive is needed for the subsequent coating. For the first time, a new generation of hydrophilic additives has been developed, which — unlike other surface additives — is able to raise the surface energy of the cured coating film substantially. This results in perfect wetting of the subsequent coating and good intercoat adhesion when recoated (Figure 1).

Results and discussion: chemistries and application results

Levelling additives are essential constituents of many coating systems, and they fulfil an important role by minimising differences in the surface tension during the drying and curing process, thus creating a smooth appearance of the surface.

The first generation of levelling additives are homopolymers or copolymers of standard alkyl acrylates or alkyl methacrylates. A (meth) acrylate monomer is a small molecule containing a polymerisable double bond that binds covalently to other monomers to build a polymer chain. The structure of the (co)polymer chain is linear. Levelling additives based on polyacrylates are slightly incompatible with the coating matrix. The polymer chains are therefore located on the surface of the coating and keep the surface tension constant during the curing process. The chemical structure and polarity can be varied within extensive limits through the selection of suitable monomers and polymerisation conditions. Setting the degree of polymerisation n determines the molecular weight, and the polarity is managed by varying the R^2 groups (Figure 2a). This first generation of structure 1 levelling additives (Table 1) has been state-of-the-art for decades.

The development of the next generations of levelling additives provides additional benefits by influencing the surface tension/energy of liquid/cured coatings. These comb copolymer structures are technically accessible through the use of special, functionalised components, the so-called "macromonomers". An acrylate macromonomer is essentially an assembly of pre-polymerised monomers modified to enable it to act as a monomer through the addition of one polymerisable double bond. The free-radical copolymerisation of standard acrylate monomers and macromonomers advantageously provides comb-shaped copolymers (Figure 2b). In this way, we designed specific acrylic comb copolymers as surface-modifying additives to dictate the surface energy of coatings, e.g. rendering their surfaces hydrophobic or hydrophilic. Silicone-modified polyacrylates have a very flexible molecular design and therefore coating properties such as hydrophobicity, oleophobicity, anti-crater performance and slip can be adjusted very precisely. Using polyether-modified polyacrylates, properties such as hydrophilicity, antistatic, antifogging, improved overcoatability and adhesion can be targeted. In the following, we will focus essentially on

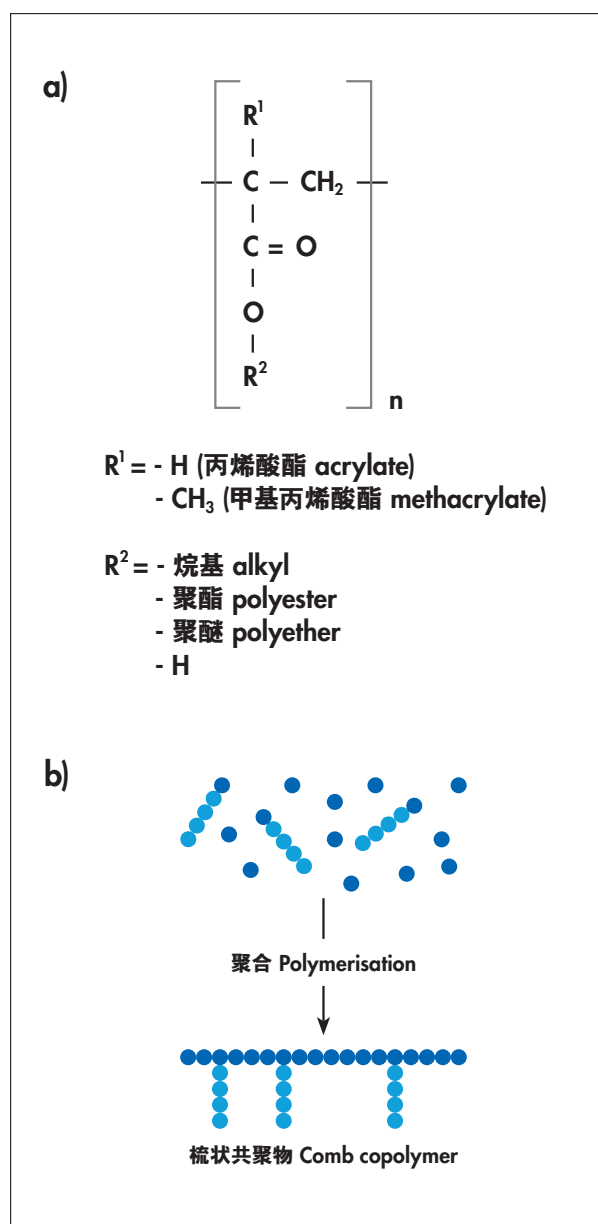





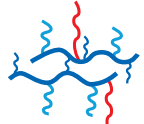


图2: a) 聚丙烯酸酯的重复单元; b) 大单体技术
Figure 2: a) Repeating units of polyacrylates;
b) Macromonomer technology

表1：传统和现代流平剂的结构图示

Table 1: Schematic structure of conventional and modern levelling additives

第一代标准聚丙烯酸酯 1st generation standard polyacrylate	流平 Levelling	线性主链 Linear chain		结构 1 Structure 1
第二代有机硅或聚醚大分子改性 2nd generation silicone or polyether-macromer modified	不影响表面能的抗缩孔作用 Anti-crater effect without influence on surface energy	线性主链和长有机硅大分子单体 Linear main chain and long silicone macromer		结构 2 Structure 2
		线性主链和长有机硅大分子单体 High surface energy and improved levelling	带有聚醚大分子单体的支化主链 Branched main chain with polyether macromer	
第三代有机硅或聚醚大分子改性 3rd generation silicone or polyether-macromer modified	高表面能和改善流平性， 轻微的防缩孔效果 High surface energy and improved levelling, slight anti-crater effect	线性主链和短有机硅大分子单体 Linear main chain and short silicone macromer		结构 4 Structure 4
		线性主链和中型有机硅大分子单体 Linear main chain and medium silicone macromer		结构 5 Structure 5
		支化主链和中等有机硅大分子单体 Branched main chain and medium silicone macromer		结构 6 Structure 6

■ 聚丙烯酸酯 Polyacrylate ■ 聚醚 Polyether ■ 有机硅 Silicone

单体」而获得。丙烯酸酯大分子单体本质上是一个预聚物，经过改性，使其能够通过添加一个可聚合双键充当单体。标准丙烯酸酯单体和大分子单体的自由基共聚有利地提供梳状共聚物（图 2b）。通过这种方式，我们设计了特定的丙烯酸梳状共聚物作为表面改性添加剂来决定涂料的表面能，例如使它们的表面疏水或亲水。有机硅改性聚丙烯酸酯具有非常灵活的分子设计，因此可以非常精确地调整涂层性能，例如疏水性、疏油性、抗缩孔性能和滑爽性。使用聚醚改性聚丙烯酸酯，可以针对亲水性、防静电、防雾、改进的重涂性和附着性等特性。在下文中，我们将主要关注亲水性添加剂。

有机硅大分子单体具有独特的分子结构，并使用受控聚合工艺生产。因此，可以针对相应的涂料体系调整这些组分的化学和物理特性——以及基于这些组分的添加剂的化学和物理特性。这也为第二代结构 2 流平添加剂（表 1）打开了大门，部分具有最初看起来矛盾的令人惊讶的特性：例如，液体涂料的表面张力大大降低，没有对固化涂层表面能的负面影响。液体涂料表面张力的显著降低通常是通过使用传统有机硅来实现的。然而，这些有机硅添加剂由于其非极性有机硅链而显著影响固化涂层的表面能。表面能的降低使重涂更加困难。

该第二代流平添加剂的另一成员可用于增加固化涂层的表面能。这种现代形式的结构 3 流平添加剂是通过开发同样高度支化的聚醚大分子单体改性结构实现的。所得亲水性添

hydrophilic additives.

The silicone macromonomers have a unique molecular structure, and are produced using a controlled polymerisation process. It is therefore possible to tailor the chemical and physical characteristics of these components — and of the additives based thereon — to the respective coating systems. This also opened the door to a second generation of structure 2 levelling additives (Table 1), with, in part, surprising characteristics that at first appear contradictory: for example, the surface tension of the liquid coating material is greatly reduced, without negative effects on the surface energy of the cured coating^[1]. A major reduction in the surface tension of the liquid coating material is normally achieved through the use of classical silicones. Nevertheless, these silicone additives significantly affect the surface energy of the cured coating on account of their non-polar silicone chain. The reduction in surface energy makes overcoating more difficult.

A further member of this second generation of levelling additives can be used to increase the surface energy of the cured coating. This modern form of structure 3 levelling additives is achieved through the development of polyether macromer-modified structures that are also highly branched. The resulting hydrophilic additives improve the levelling, and bring about an increase in the surface energy of the cured coating. The result is a significantly improved overcoatability^[2].

The next generation of structures 4, 5 and 6 levelling additives have been developed in order to combine the said beneficial characteristics in a single product. This third generation uses the full spectrum of macromonomer

加剂改善了流平性,并增加了固化涂层的表面能。结果是显著改善的重涂性。

已开发出下一代结构 4、5 和 6 流平添加剂,以便在单一产品中结合上述有益特性。第三代使用全谱大分子单体技术,从而可以实现独特的结构和性能。亲水性聚醚和疏水性有机硅大分子单体的结合导致了新型流平助剂的开发,这些助剂可以改善重涂性和流平性,同时还具有抗缩孔性能。因此,第三代和下一代代表了流平添加剂历史上的一个里程碑。

为了更好地说明新添加剂的效果,表 1 从应用角度比较了 3 代的各种添加剂结构及其特性。

下一代添加剂在基于聚酯和三聚氰胺基料的传统 1K-OEM 底漆中进行了测试,并与经典有机硅添加剂或标准丙烯酸酯流平添加剂进行了比较。结果总结在图 3 中。

使用拉环法测量液体涂料的表面张力表明,只有具有较长有机硅链的添加剂(经典有机硅添加剂和含有有机硅大分子单体的结构 2 流平添加剂)才能显著降低表面张力。具有较短有机硅链的结构(例如结构 4)以及两种不含有机硅的添加剂(结构 1 和结构 3)对表面张力降低没有或只有很小的影响。

虽然经典的有机硅添加剂降低了表面张力,但结构 5 和 6 的基于有机硅大分子单体的流平添加剂并没有显著降低表面张力,尽管它们的结构中含有有机硅。基于聚醚大分子单体的流平添加剂 3 与底漆非常相容,它几乎不会将自身定向到涂层/空气界面,因此仅略微增加固化涂层的表面能。然而,如 4、5 和 6 结构那样,一旦包含聚醚大分子结构,同时也包含有机硅大分子结构时,它们就会更强烈地朝向界面定向迁移——这一事实清楚地反映在测得的更高表面能中。

technology, thus making it possible to achieve unique structures and properties. The combination of hydrophilic polyether and hydrophobic silicone macromonomers has resulted in the development of levelling additives that offer improved overcoatability and levelling, and also anticrater performance. The third and next generation therefore represents a milestone in the history of levelling additives.

To better illustrate the effects of the new additives, **Table 1** compares the various additive structures of the 3 generations and their properties from an application perspective.

The next generation additives were tested in a conventional 1K-OEM primer based on polyester and melamine binders, and compared with classical silicone additives or standard acrylate-based levelling additives. The results are summarised in **Figure 3**.

A measurement of the surface tension of the liquid coatings using the du Noüy ring method shows that only additives with longer silicone chains (classical silicone additive and structure 2 levelling additives containing silicone macromonomers) can achieve a significant reduction in the surface tension. Structures with shorter silicone chains such as structure 4 as well as the two silicone-free additives (structure 1 and structure 3) show no or only very minor effects on the surface tension reduction.

While the classical silicone additive reduces the surface tension, the silicone macromer-based levelling additives of structures 5 and 6 do not reduce surface tension substantially, despite silicone in their structures. The polyether macromer-based levelling additive 3, which is very compatible in the primer, hardly orientates itself towards the coating/air interface, and thus only slightly increases the surface energy of the cured coating. However, as soon as the structures that contain polyether macromonomer also combine silicone macromonomer as in structures 4, 5 and 6, they orientate

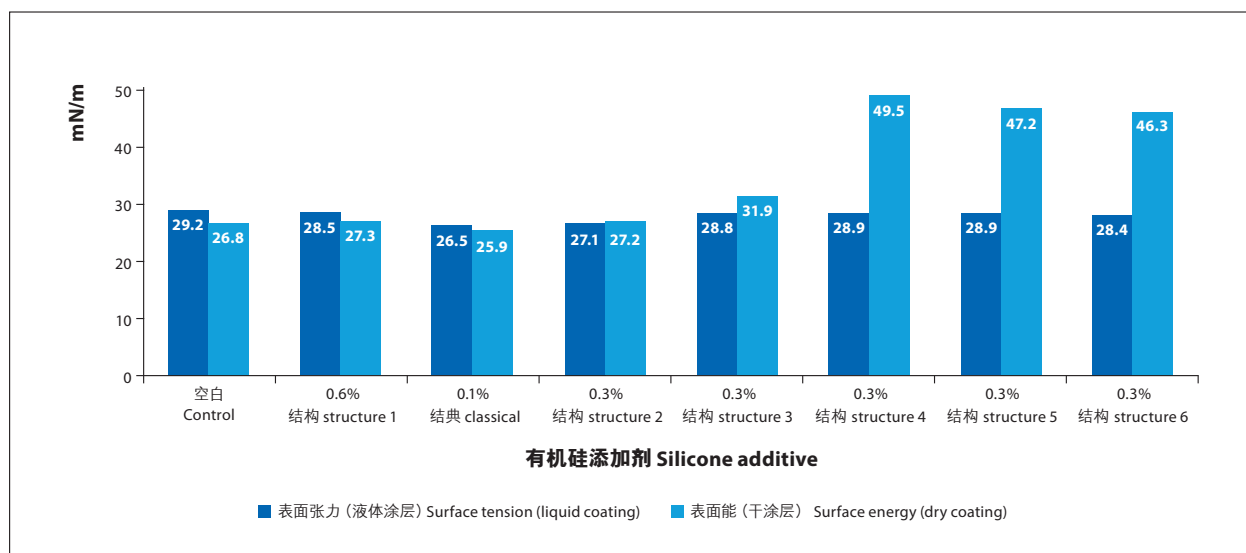


图3: 测量传统OEM汽车底漆的表面张力和表面能。

测试系统: 基于Setal® 1671 SS-65、Setamine® US-138 BB-70、Epikote® 1001的溶剂型底漆。

测试方法: 在电泳涂装样板上旋杯喷涂, 固化条件: 10分钟, 160°C, 闪干20分钟。

Figure 3: Measured surface tensions and surface energy of a conventional OEM automobile primer.

Test system: solventbased primer based on Setal® 1671 SS-65, Setamine® US-138 BB-70, Epikote® 1001.

Test method: bell application on electro-coated sheets, curing conditions: 10 min. flash-off, 20 min. at 160 °C.

即使更低固化温度下也能提高效率

由于聚醚大分子单体的良好相容性，结构 3 添加剂在常规和水性体系中均表现出不足的表面取向。

在室温或低温固化的水性体系中，具有结构 3 的添加剂通常不会在表面充分迁移以实现表面能的显著增加。从图 4 中可以看出，在机构 4 和 6 中，通过调整有机硅大分子和聚醚大分子的组合可以获得更显著的效果。尽管有机硅链更长，但结构 6 的添加剂比结构 4 的添加剂导致更大的表面能增加，这一事实似乎是矛盾的。这是因为有机硅链越长，添加剂越不相容，从而有利于它们迁移至涂层—空气界面。

时刻关注波纹度

新结构在水性面漆系统中也很有趣。这些系统中底层涂层的润湿通常是通过传统的有机硅添加剂产生的。这些添加剂通常也用于使涂层具有抗缩孔性并形成光滑的表面。

事实上，这些经典的有机硅会导致表面能降低。尽管这对单一涂层并不构成问题。然而，如果为了修补或实现光学外观（例如双色饰面）而必须再次重涂面漆，则较低的表面能不仅会导致润湿性变差，而且流平性也会变差，同时较短有机硅链的添加剂（结构 4）显示摩擦系数没有降低（没有增加表面清爽），但具有较长有机硅链（结构 5 和结构 6）的添加剂导致显著的表面清爽增加（图 5）。

通过面漆的应用也可以证明总表面能增加的趋势。由于结构 5 和结构 6 添加剂的更好表面取向，总表面的极性部分随着有机硅链的长度增加明显增加（图 6）。

结论

我们讨论了一种「新」方法，该方法包括使用亲水性添加剂来增加底层涂层的表面能，从而对后续涂层的润湿产生积极影响。该技术主要推荐用于所有类型的多层涂装系统。最

themselves more strongly towards the interface — a fact that is clearly reflected in the higher surface energies measured.

Increased effectiveness even at lower curing temperatures

Due to the good compatibility of the polyether macromer, the structure 3 additive showed insufficient surface orientation in both conventional and waterborne systems.

In waterborne systems, which are cured at room temperature or at low temperature, the additive with structure 3 often does not orient sufficiently at the surface to achieve a substantial increase in surface energy. As can be seen in Figure 4, a considerably greater effect can be achieved in these systems with the combined silicone macromonomer and polyether macromonomer structures 4 and 6. The fact that the additive with structure 6 causes a greater increase in the surface energy than the additive with structure 4 despite longer silicone chains, appears contradictory. This is due to the additives becoming increasingly more incompatible the longer the silicone chain, and thus favoring their orientation towards the coating-air interface.

An eye on the waviness at all times

The new structures are also interesting in hydro topcoat systems. The wetting of the underlying coating in these systems is usually produced by means of classical silicone additives. These additives are normally used to make the coating crater-resistant as well and create a smooth surface.

In fact, these classical silicones cause a reduction in the surface energy. This does not however constitute a problem with single coating. Nevertheless, if the topcoat has to be overcoated again for the purpose of repair or optical appearance (for example two-colour finish), the lower surface energy causes not only poorer wetting but also poorer levelling. While the additive with the shorter silicone chain (structure 4) showed no reduction in coefficient of friction (no increase of surface slip), the additives with longer silicone

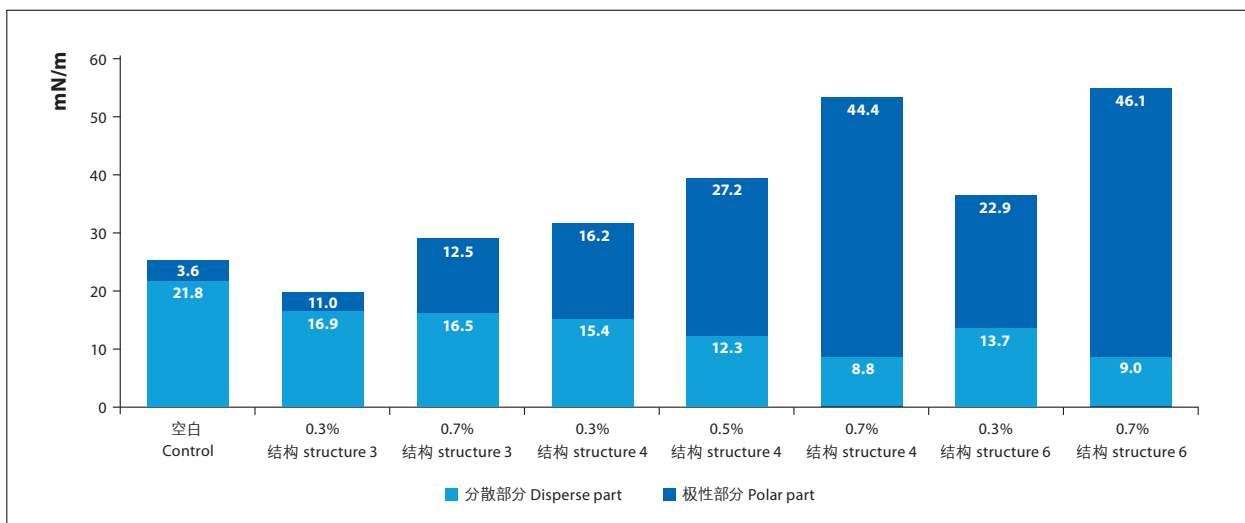


图4：在 80°C 下固化 10 分钟后测量水性底漆的表面能。

Figure 4: Measured surface energy of a waterborne basecoat after curing for 10 minutes at 80 °C.

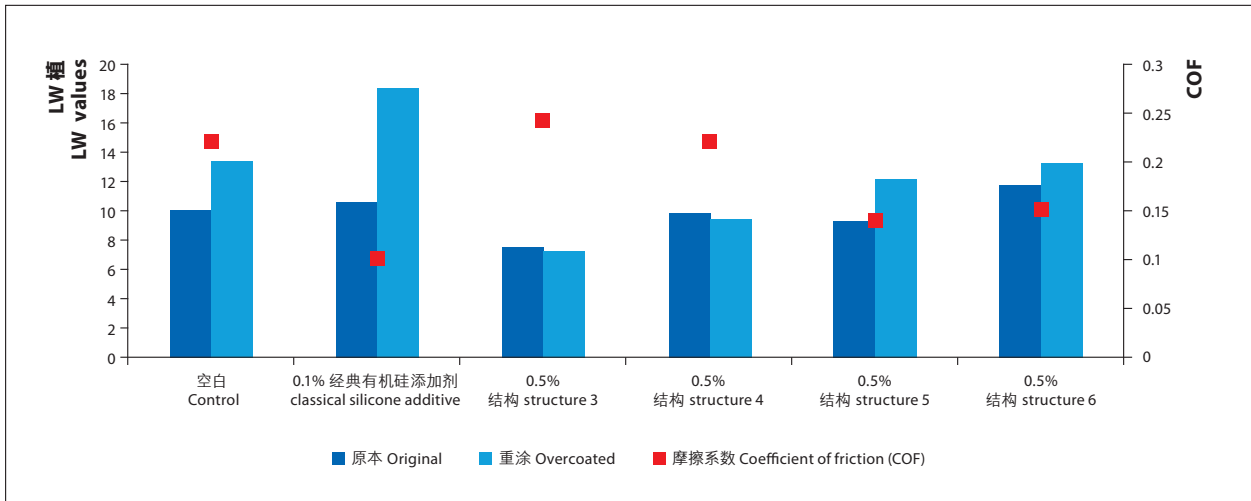


图5：直接测量旋杯喷涂白色水性面漆以及修补后的涂层的流平和滑爽性。

Figure 5: Measurement of the levelling of bell applied white water-based topcoat directly and after repair with itself, and slip measurement of these coatings.

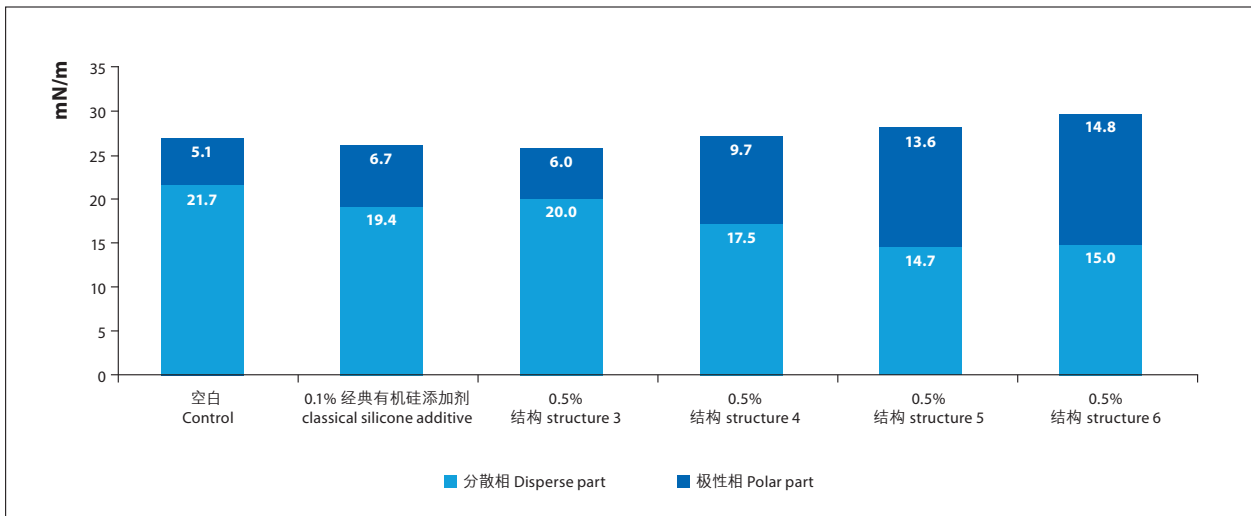


图6：静电喷涂白色水性面漆的表面能测量值。

Figure 6: Measured surface energy of an ESTA-coated white water-borne topcoat.

新一代的亲水添加剂是多功能的，可以结合抗缩孔行为和增加亲水效果以及滑爽性等特征。

参考文献 References

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chains (structure 5 and structure 6) caused a significant surface slip increase (Figure 5).

The trend of an increase in the overall surface energy can also be demonstrated with the topcoat. The polar part of the total surface clearly increases with the length of the silicone chains due to better surface orientation of the structure 5 and structure 6 additives (Figure 6).

Conclusion

We discussed a "new" approach that consists using hydrophilic additives to increase the surface energy of an underlying coating, which positively affects the wetting of the subsequent coating layer. The technology is recommended for principally all types of multilayer coating systems. The latest generation of hydrophilic additives are multi-functional and can combine properties such as anticratering behaviour and increased slip to the hydrophilic effects. ☐