丙烯酸弹性屋顶防水涂层用硅烷改性胶体二氧化硅 **性能增强剂**

Silane Modified Colloidal Silica as **Performance Enhancer** of Acrylic Elastomeric Roof Coatings

在丙烯酸弹性体屋顶防水涂层配方中加入硅烷改性胶体二氧化硅时，许多性能得到了提升。配方中加入 2.2-2.8%（等于产品的 8-10%）的二氧化硅达到性能的最佳水平。

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结果表明，在涂层中对疏水及亲水性的污垢耐污性显著提高。此外，即使在 UV 室中经加速老化 1,000 小时后，效果也仍能保持。令人惊讶的是，还改善了配方产品的罐内稳定性，特别是在 50℃ 下储存，此温度是温暖国家的仓库中可以达到的温度。

对于新鲜涂层和老化后涂层中均发现：在不牺牲涂层柔韧性的情况下，涂层的力学性能和附着力都得到极大的提高。

A number of properties were enhanced in acrylic elastomeric roof coatings upon addition of silane modified colloidal silica in the formulation. A dosage in the range of 2.2-2.8% SiO_2 (equal to 8-10% product) on formulation appeared to be optimal level. The results showed dramatic enhancement of dirt pick-up resistance in fresh stage, both for hydrophobic and hydrophilic dirt. In addition, the effect was long lasting even after 1,000 hours of accelerated weathering in UV chamber. Surprisingly, the in-can stability of the formulation was improved, especially at storage at 50℃, that is a temperature that can be reached in warehouses in warm countries. Strong improvement in mechanical properties and adherence of the coatings without sacrificing coating flexibility for both fresh and aged coatings were also found. Furthermore, the addition of silane modified colloidal silica did not affect the Total Solar Reflectance (TSR) value or causes any degradation of coating film, which is important when used in so called cool roof coatings.

Introduction

Increasing the solar reflectance (albedo) of roofs can cool buildings, reduce air conditioning use[1-4] and lower city-wide outdoor air temperatures[5-10]. From a global perspective, increasing the average albedo of existing urban areas can

此外，加入硅烷改性胶体二氧化硅不会影响总太阳反射（Total Solar Reflectance, TSR）值或导致涂膜的任何降解，这在降温屋顶防水涂层中的使用非常重要。

引言

增加屋顶的太阳能反射值（Albedo）可以使建筑物凉爽，减少空调使用[1-4]和降低城市的室外空气温度[5-10]。从全球性的角度来看，增加现有城市地区的平均太阳能反射值会通过减少地球吸收的辐射来部分抵消气候变化[11-14]。

凉爽的屋顶防水涂层有助于减少建筑物的升温，主要是由于其高的太阳能反射特性。通过减少建筑物中的冷却能源使用，我们有可能降低发电厂排放，显著缓解了配电问题并节省了电力。空调的能量消耗集中到一天的几个小时，峰值能量需求对配电系统带来很大的压力。不仅是电力分布问题，而且高能耗带来高成本，并且当化石燃料用于产生能量时[15]，大气中的二氧化碳水平也会增加。凉爽的屋顶防水涂层主要设计用于反射太阳中能量的主要部分，通常通过添加反射颜料如二氧化钛（TiO₂）起到作用[16]。

屋顶防水涂层有很多要求，不仅要求高度反射，而且由于存在较大的温度差异也要非常有韧性，即弹性。此外，由于太阳曝晒的苛刻条件，这类涂层需要具有非常好的耐紫外线性能，同时也需要良好的附着力和耐水性（由于屋顶上有水池）。这些要求在例如 ASTM D-6083 标准中有详细描述。由于其弹性性质，这种涂料非常容易被污垢污染，特别是新鲜涂层的状态。污垢的堆积对反射率非常有害，对白色凉爽屋顶防水涂层的效率也很有害处；暗色涂层比白色更温暖。一种提高抗污性能的众所周知的方法是通过改性树脂使其硬度更高，即增加树脂的玻璃化转变温度。然而，这种方法在涂料的柔韧性上存在缺陷，通常牺牲了韧性。因此，在不降低柔韧性或涂层其它性能的情况下，提高耐沾污性能具有重要的需求。

硅烷改性胶体二氧化硅可用于涂料中提高耐沾污性能[17-19]，但关于弹性屋顶防水涂层中二氧化硅的影响报导很少。人们可以期望耐沾污性能方面会产生良好的影响，但对诸如罐内配方稳定性，涂层柔韧性和强度，涂层的抗紫外线，附着力和反射性能等参数的影响，到目前为止尚未开展研究。在本研究中，测试了胶体二氧化硅对上述参数的影响。研究中采用的基础涂层配方应用的是陶氏化学开发的基于丙烯酸树脂的 ARM-91。

实验部分

参考配方

表1显示，基于 ARM-91-D1 弹性屋顶防水涂料参考配方，以 Rhoplex / Primal EC-1791 丙烯酸树脂为基料。

配制方法

实例的配制使用相同品质的颜料（二氧化钛和氧化锌），并保持配方的 PVC（颜料体积浓度）恒定为 43.1%，以及总固体含量为 63.84%。加入胶体二氧化硅后，配方中相应减少碳酸钙填料和加入水。所制备的配方中硅烷改性胶体二氧化硅分别占总配方品质的 6wt-%、8wt-%、10wt-% 和 12wt-%。使用的硅烷改性胶体二氧化硅 Levasil CC301，粒径为 7nm 和二

partially counteract climate change by reducing the radiation absorbed by the Earth.[11-14]

Cool roof coatings help reduce the heat up of buildings mainly thanks to their high solar reflecting properties. By reducing the cooling energy use in buildings, we have the potential to reduce power plant emissions, significantly ease the power distribution problem and save money on electricity. Energy consumption by AC is concentrated to a few hours of the day and the peak energy demand puts high stress on power distribution systems. Not only is it a power distribution problem, but the high energy consumption also causes unwanted cost and contributes to increase of CO_2 levels in the atmosphere when fossil fuels are used for energy production[15]. Cool roof coatings are designed to reflect significant parts of the energy from the sun, often aided by the addition of a reflecting pigment like titanium dioxide (TiO_2)[16].

There are many demands on a roof coating, it should be not only highly reflective, but also very flexible, i.e. elastomeric, due to big temperature differences. Further, this kind of coating must have very good UV resistance due to harsh conditions of sun exposure, good adhesion as well as good water resistance (due to water ponding on roof). The requirements are detailed in e.g. the ASTM D-6083 standard. Due to its elastomeric nature, this kind of coatings are very prone to dirt pick-up, especially in their fresh state. Dirt pick-up is extremely detrimental for the reflectivity and hence for the efficiency of white cool roof coatings; a dark coating becomes much warmer than a white one. One well-known way of enhancing dirt pick-up resistance is to modify the resin by making it harder, i.e. increasing the T_g of the resin. However, this approach has the draw-back that coating flexibility normally is sacrificed. There is therefore a big need for enhancing dirt pick-up resistance without reducing flexibility or coating performance otherwise.

Silane modified colloidal silica is used to enhance dirt pick-up resistance in paints,[17-19] but little is known about the effect of silica in elastomeric roof coatings. One could expect a good effect on dirt pick-up resistance but the influence on parameters such as in-can formulation stability, coating flexibility and strength, UV resistance of the coating, adhesion and reflective properties have up till now not been studied. In this study, the influence of colloidal silica addition on the above-mentioned parameters has been tested. As the basis from formulation point-of-view, a coating formulation, ARM-91 (developed by DOW), based on an acrylic resin has been used.

Experimental

Reference formulation

Table 1 shows the reference formulation based on ARM-91-D1 Elastomeric Roof Coating Formulation with Rhoplex/Primal EC-1791 acrylic binder.

Formulation approach

The examples were formulated to use the same mass of pigment (TiO_2 and ZnO), and to maintain a constant PVC (pigment volume concentration) of 43.1% as well as solid content of 63.84% by weight of the formulation. Upon colloidal silica addition, a corresponding reduction in the calcium carbonate filler and additional water was made. The formulations with silane modified colloidal silica were prepared with 6 wt-%, 8 wt-%, 10 wt-% and 12 wt-% product

表1：基于ARM-91-D1弹性屋顶防水涂料参考配方，以Rhoplex／Primal EC-1791丙烯酸树脂为基料
Table 1: Reference formulation based on ARM-91-D1 Elastomeric Roof Coating Formulation with Rhoplex/Primal EC-1791 acrylic binder

组分 Component	商用名 Commercial name	重量 Weight (g)
研磨料 Mill-Base		
水 Water	PCI #7	152.50
分散剂 Dispersant	Orotan™ 851	1.60
分散剂 Dispersant	KTPP (1)	1.40
消泡剂 De-foamer	DAPRO™ 7580	1.90
碳酸钙 Calcium carbonate	Snowhite™ 12	422.20
二氧化钛 TiO₂	Kronos ™ 2160	90.00
氧化锌 Zinc oxide	Zoco™ 101	20.00
分散料 Let-Down		
乳液基料 Binder-Latex (丙烯酸乳液 acrylic emulsion)	Primal™ EC-1791	470.60
消泡剂 De-foamer	DAPRO™ DF 7005	1.90
助溶剂 Solvent (丙二醇单酯 propanediol monoester)	DAPRO™ FX 511	7.00
杀菌剂 Mildewcide (真菌杀灭剂 Fungicide)	Acticide™ MBS	2.10
杀菌剂 Mildewcide (真菌杀灭剂 Fungicide)	Acticide™ MKW2	1.20
助溶剂 Solvent (丙二醇 propylene glycol)		24.40
邻苯二甲酸二异壬酯 Diisononyl phthalate (DINP)	Jayflex™ DINP	3.00
1,2-环己烷二羧酸二异壬酯 Cyclohexane dicarboxylic acid diisononyl ester	Hexamoll™ DINCH	35.00
疏水改性的羟乙基纤维素 Hydrophobically modified ethylhydroxycellulose	Bermocoll™ EBM 8000	4.20
合共 Total		**1,239**
总固体含量 Total Solid content (wt%)	63.84%	
颜料体积浓度 Pigment Volume Concentration	43.1%	

(1) 焦磷酸钾 Potassium tetrapyrophosphate

氧化硅含量为 28wt-%，使涂层胶膜中二氧化硅的含量分别为 1.68wt-%、2.24wt-%、2.80wt-% 和 3.36wt-% 的不同水平。研磨料采用 NIEMANN Kreis Dissolver 分散机分散 10 分钟，转速 2,500 转／分钟，径向速度约为 25 米／秒。分散料在 850 转／分钟下轻轻搅拌。

粘度

根据 ASTM D2196 使用旋转粘度计来测量组合物的动态粘度（布鲁克菲尔德型）粘度计。

涂料配方稳定性

在初始时和在室温下储存 1 个月后测量涂料组合物的动态粘度。还将单独的样品储存在 50℃ 下 1 个月后测量其动态粘度。使用配备有铝合金锥板块几何形状的流变仪的「Discovery HR2」（1.59°，直径：40mm，间隙：56μm），以 1s-1 的剪切速率测量粘度（Pa s）。

加速老化测试

根据 ISO 16474-2 将样品进行 1,000 小时加速老化储存。将样品涂装到铝基板上并在 23℃ 和 50% 相对湿度下允许干燥 14 天，然后使用 MinoltaCr-200 Tristimulus 比色计进行初始测量。然后在 Q-SUN XE 3 HS 耐候测试仪装置中经过滤的氙弧灯照进行 1,000 小时加速老化，然后再进行分析。

additions by weight on total formulation. The silane modified colloidal silica used, Levasil CC301, has a particle size of 7 nm and SiO_2 content of 28 wt%, giving an addition of SiO_2 to the coating film of 1.68, 2.24, and 2.80 and 3.36 wt% respectively for the different addition levels of product. Millbase was dispersed with NIEMANN Kreis Dissolver for 10 min at 2,500 rpm, radial velocity around 25 m/s. Let down was made with gentle agitation at 850 rpm.

Viscosity

Dynamic viscosities of the compositions were measured, according to ASTM D2196, using a rotational (Brookfield type) viscometer.

Stability of coating formulation

The dynamic viscosity of the coating composition was measured initially, and after 1-month storage at room temperature. A separate sample was also kept at 50°C for 1 month, before its dynamic viscosity was also measured. Viscosities (Pa s) were measured at a shear rate of 1 s^{-1} using rheometer 'Discovery HR2' equipped with cone-plate geometry in aluminium (1.59°, diameter=40 mm, gap=56 μm).

Accelerated ageing test

Samples were subjected to accelerated ageing conditions over 1,000 hours, according to ISO 16474-2. Samples were initially applied to an aluminium substrate and allowed to dry for 14 days at 23°C and 50% relative humidity, at which

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对新配制和经老化后的涂层进行测量。涂层通过两层涂装间隔时间为 4 小时制备得到，以提供 500±50μm 的干燥膜。7 天后将涂膜从基材上剥离下来，并在剩馀的干燥和老化过程中静置在基板上。

使用方法 ASTM D2370 测量断裂伸长率和拉伸强度（最大应力）。对基材上剥离的涂膜，可直接或在 1,000 小时后进行测量。干膜厚度约为 500μm 厚度，切成 7.5×1.3cm 的片状进行测试。在测试前 1.3 厘米。将切割得到的涂膜夹在夹具的两端，夹具之间具有 25mm 的距离。夹具以 25±0.5mm/min 的速率分开，直至薄膜撕裂。还测量了最大阻力的点。使用的设备是 Instron™ 3355 通用测试机。

抗撕裂性

使用与上节「拉力及强度性能」中的相同装置，按试验方法 ASTM D624 测量最初干燥的涂层（厚度）的抗撕裂性。夹具以 500mm/min 的速率分开。

低温柔韧性

根据 ASTM D522，使用锥形轴弯曲试验测量铝基板上的涂层的柔韧性。膜厚度约为 360μm。涂装后，将它们在 23℃和 50% 相对湿度下干燥 72 小时，然后按「加速老化测试」一节中描述的条件下老化。老化后，在进行测量之前，将样品在 50℃和 50% 相对湿度下调节 120 小时，然后在 -26℃ 下存放一天。测试中，涂装的基材在一系列下降的轴上弯曲。结果以最小轴的直径来确定，要求没有可见裂缝出现。

耐沾污性能

通过氧化铁和炭黑水基糊状物弄脏涂覆的铝样板。这些浆料仅含有水和氧化铁／炭黑颜料，没有任何其它添加剂。将浓缩的污渍浆料置于待评估的表面上，并使其干燥 24 小时。首先用软毛巾用水冲去干燥的斑点。在第二步中，表面也通过带水和肥皂的软毛巾洗涤表面，以模拟雨水和清洁过程。对新涂布的表面和经过表面污染和洗涤的涂装表面采用三色座标 (L，a, b) 进行测试，使用「加速老化测试」一节中的 Tristimulus 比色计进行测试。然后计算「清洁后」和「污染前」涂层之间的总色差值值 ΔE。低 ΔE 值对应于高耐沾污性能。同时对在室温下干燥 1 个月后的涂层，以及按「加速老化测试」一节中方式进一步老化 1,000 小时的样品进行耐沾污性能测试。

附着力

根据试验方法 ASTM D903 和 ASTM C794 进行湿态和干态附着力试验。用刷涂涂装到镀锌钢板基材上。然后将 2.5cm 宽的布料置于顶部，随后涂布另一种涂层。干燥时间为 23℃/50% 相对湿度为 14 天。总涂层厚度约为 500μm。

对于干态附着试验，将试样条带以 50mm/min 的牵引率以 180°角向后拉，测量所需的力。同样地进行湿粘附试验，但在将样品浸入室温自来水中 168 小时后进行测试。

point initial measurements were made using a Minolta CR-200 tristimulus colourimeter. They were then subjected to 1,000 h accelerated ageing under a filtered xenon arc lamp in a Q-Sun Xe 3 HS weathering tester apparatus before being re-analysed.

Tensile and strength properties

Measurements were made on fresh and aged coatings. Coatings were formed by applying two coats at a 4-hour interval, to provide a dried film of 500 ± 50 μm. The films were peeled off their substrates after 7 days, and allowed to rest on the substrate for the remainder of the drying and ageing process.

Elongation at break and tensile strength (maximum stress) were measured using ASTM D2370 method. Measurements were made on films detached from the substrate, either directly or after 1,000 h ageing. The dry film thickness was approximately 500 μm and was cut into pieces measuring 7.5 x 1.3 cm before being tested. The piece of cut film was clamped at each end, with a 25 mm distance between the clamps. The clamps were moved apart at a rate of 25±0.5 mm/min until the film split. The point of maximum resistance to moving the clamps was also measured. The device used was an Instron™ 3355 universal test machine.

Tear resistance

Using the same apparatus as in previous section of "Tensile and strength properties", the tear resistance of an initially dried coating (500 μm thickness) was measured following test method ASTM D624. The clamps were moved apart at a rate of 500 mm/min.

Low temperature flexibility

The flexibility of coatings on an aluminium substrate was measured using a conical mandrel bend test, according to ASTM D522. The film thickness was approximately 360μm. After application, they were allowed to dry for 72h at 23°C and 50% relative humidity, followed by ageing under the conditions described in the "Accelerated ageing test" section.

After ageing, and before measurements were made, the samples were conditioned for 120 h at 50°C and 50% relative humidity, followed by one day at -26°C. In the test, the coated substrate is bent over a series of mandrels of decreasing diameter. The result is based on the lowest mandrel diameter at which no crack is visible.

Dirt pick-up resistance

Coated aluminium substrates were soiled by means of iron oxide and carbon black water based pastes. Those pastes contained only water and the iron oxide/ carbon black pigment without any other additives. The concentrated soiling pastes were placed on the surface to be characterised and were allowed to dry for 24h. The dried cakes were firstly removed under running water using a soft towel. In a second step, the surface was also washed by means of a soft towel with water and soap, to simulate rain and cleaning. Trichromatic coordinates (L, a, b) were measured initially and after soiling and washing of the paint surfaces, using the tristimulus colourimeter set out in the "Accelerated ageing test" section. The total colour change value, ΔE between the "cleaned" and the "pre-soiled" coating was then calculated. Low ΔE values correspond to high dirt pick-up resistance.

吸水率

吸收率，根据试验 ASTM D471，测试干燥涂膜（在 23℃/50% 相对湿度下干燥 14 天）浸入水中 168 小时后吸收水分的品质增长比率。

水蒸气渗透性

根据 ASTM D1653 测试水蒸气渗透性，首先制备新鲜干燥（在 23℃/50% 相对湿度下干燥 14 天）的游离涂膜。在仪器中测量渗透值，并且使用 1.51735 的转换因数来计算美国单位值。

太阳能反射

在室温和 50% 湿度下干燥 1 个月的铝基材板涂装样板上，测量波长在 280 至 2,500nm 范围内的反射率，如「加速老化测试」一节所述，进一步对 1,000 小时老化储存的涂装样板进行测量。干膜厚度在 236-340μm 的范围内。使用 ASTM E903 测试方法，以 ASTM G173 为参考。所用的装置是 Agilent Cary 5000 紫外可见光光谱仪。

扫描电镜 / 能谱测试

扫描电子显微镜（SEM）采用 JEOL 780°F 仪器对样品的表面和横截面进行测试。在 SEM 下观察之前，通过在 20kV 的加速电压下对样品进行钯溅射涂布预处理，能量色散 X 射线光谱，EDS，也是按类似的技术进行样品准备，用相同的仪器进行测试，测量表面和横截面的元素组成（C、O、Si、Ti、Zn、Ca）。

结果
粘度

表 2 列出各配方在 ASTM D2196 动态粘度测量的数据。屋顶丙烯酸涂层的动态粘度要求（根据 ASTM D6083）是 12 至 85Pa s。

涂料配方稳定性

表 3 显示粘度对时间、剪切速率：1/s 的测量结果。结果表明，与不含硅烷改性胶体二氧化硅的组合物相比，改性样品显示出更优的长期稳定性（粘度增长较小）。

加速老化测试 (1,000 小时)

表 4 显示 L、a 和 b 值以及 **ΔE** 值。总色彩变化：ΔE 表示根据下面等式的老化前后的 L，a 和 b 值的差异：$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$。所有配方均具有良好的耐紫外线性能；没有变黄 / 涂层劣化（b 值未增加）。所有样品的颜色变化非常小。

拉力及强度性能

表 5 显示杨氏模量、断裂伸长率和最大拉伸强度。硅烷改性胶体二氧化硅改善了初始和长期拉伸强度和杨氏模量，且

The dirt pick-up resistance was measured for fresh coatings after 1 month of drying at room temperature as well as for samples aged for a further 1,000 h in the way set out in the "Accelerated ageing test" section.

Adhesion

Wet and dry adherence tests were made according to test methods ASTM D903 and ASTM C794. A coating was applied by brush to a galvanised steel substrate. A 2.5cm wide strip of cloth was then placed on top, and another coating layer subsequently applied. Drying time was 14 days at 23℃ / 50% relative humidity. Total coating thickness was ca. 500 μm.

For the dry adherence test, the strip was pulled backwards at a 180° angle at a traction rate of 50 mm/min, and the force required to do so was measured. The wet adherence test was carried out similarly, but after the sample had been immersed in tap water for 168 hours at ambient temperature.

Water uptake

Uptake of water, as increase of film weight in wt%, into free films of the freshly dried coatings (14 days at 23℃/50% relative humidity) was measured according to test method ASTM D471 with immersion 168 hours in water.

Water vapour permeability

Water vapour permeability tests according to ASTM D1653 were conducted on free films (i.e. after removal from substrate) of freshly dried coatings, i.e. after 14 days drying at 23℃/50% relative humidity. Perms values were measured in metric units and the US values were calculated using a conversion factor of 1.51735.

Solar reflectance

Reflectance of wavelengths over the 280-2,500 nm range were measured on aluminium-coated substrates, one month after drying at room temperature and 50% humidity, and on coated substrates aged for a further 1,000 h as described in the "Accelerated ageing test" section. Dry film thicknesses were in the range of 236-340 μm. The ASTM E903 test method was used, with ASTM G173 reference. The apparatus used was an Agilent Cary 5000 UV-visible spectrometer.

SEM/EDS

Scanning electron microcopy (SEM) was used to observe the surface and the cross sections of the samples using a JEOL 780°F Prime instrument. Samples were pre-coated with palladium by sputtering at an accelerating voltage of 20kV before observing under SEM. Energy-Dispersive X-ray Spectroscopy, EDS, was also carried out in the same instrument with similar sample preparation technique to measure the elemental composition (C, O, Si, Ti, Zn, Ca) of the surfaces and cross-sections.

Results

Viscosity

Table 2 shows the dynamic viscosity measurements ASTM D2196 of different formulations. The requirement for acrylic coatings for use in roofing (according to ASTM D6083) is for a dynamic viscosity of 12-85 Pa s.

断裂伸长率性能不会显著降低。根据 ASTM D6083，在 1,000 小时的加速老化后，断裂伸长率值需要在 100% 或更高的水平。

抗撕裂性

表 6 显示 ASTM D624 测试方法的抗撕裂性能测试数据。添加胶体二氧化硅提高了涂层的抗撕裂性，使涂层更坚韧。

低温柔韧性

表 7 显示锥形心轴柔韧性。为了在低温下获得良好的柔韧性，ASTM D6083 规定最大直径值为 13 毫米。该参数在环境温度的大和 / 或快速变化的区域中非常重要。所有测试的配方符合低温柔韧性的要求。

新制备涂料的耐沾污性

表 8 显示耐沾污性能测试，L、a、b 和 **ΔE** 值。加入硅烷改性胶体二氧化硅可显著降低污染堆积，并且针对疏水性（炭黑）和亲水性（氧化铁）污垢均有效（**图 1**）。

Coating formulation stability

Table 3 shows the measurements of viscosity over time, shear rate, 1/s. The results show that the modified samples show improved long-term stability (less increase in viscosity) compared to the composition comprising no silane modified colloidal silica.

Accelerated ageing test (1,000 hours)

Table 4 shows L, a, b and ΔE values. The total **4** colour change; ΔE represents the differences in the L, a and b values before and after ageing according to the following equation: $\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$. All formulations have good UV resistance; no yellowing /coating degradation (b-values are not increased). It can be seen, from **Table 4**, that the total colour change is very small for all samples.

Tensile and strength properties

Silane modified colloidal silica improves both the initial and long-term tensile strength and Youngs Modulus, without any significant reduction in the elongation at break performance. For ASTM D6083, a value for elongation at break of 100% or higher is required after 1,000 h of accelerated ageing (**Table 5**).

Tear resistance

Table 6 shows the tear resistance test method ASTM D624. Clearly, the addition of colloidal silica improved tear resistance making the coating tougher.

Low temperature flexibility

Table 7 shows the conical mandrel flexibility. To obtain good flexibility at low temperatures, ASTM D6083 stipulates a maximum diameter value of 13mm. This parameter is important in areas where there are big and/or fast changes

表2：ASTM D2196动态粘度测量
Table 2: Dynamic Viscosity Measurements ASTM D2196

配方 Formulation	粘度 Viscosity (Pa s) 布氏/ 4号转子 / 6转/分钟 Brookfield / spindle 4 / 6rpm
参照样 Reference	32.97
参照样 Reference + 1.68 % SiO₂	22.23
参照样 Reference + 2.24 % SiO₂	22.37
参照样 Reference + 2.80 % SiO₂	22.37
参照样 Reference + 3.36 % SiO₂	16.27

表3：粘度对时间、剪切速率: 1/s 的测量结果
Table 3: Measurements of viscosity over time, shear rate: 1/s

流变数据 Rheometer data	23°C时的初始粘度 (Pa s) Initial Viscosity, (Pa s), at 23°C	23°C存放1个月后的粘度 (Pa s) Viscosity (Pa s) after 1 month, at 23°C		50°C存放1个月后的粘度 (Pa s) Viscosity (Pa s) after 1 month, at 50°C	
			粘度变化 Viscosity change		粘度变化 Viscosity change
参照样 Reference (Ref)	34.39	39.58	5.19	45.97	11.58
参照样 Ref + 1.68 % SiO₂	22.72	23.00	0.28	23.85	1.13
参照样 Ref + 2.24 % SiO₂	21.19	23.56	2.37	23.38	2.19
参照样 Ref + 2.80 % SiO₂	22.84	23.84	1.00	26.73	3.89
参照样 Ref + 3.36 % SiO₂	17.07	18.46	1.39	19.91	2.84

表4：L、a和b值以及ΔE 值
Table 4: L, a and b values as well as delta E

配方 Formulation	初始值 Initial			加速老化后的值 Post ageing			ΔE
	L	a	b	L	a	b	
参照样 Reference (Ref)	96.49	-0.80	1.32	96.81	-0.79	1.34	0.32
参照样 Ref + 1.68 % SiO₂	96.97	-0.79	1.32	96.52	-0.77	1.35	0.45
参照样 Ref + 2.24 % SiO₂	96.81	-0.82	1.15	96.59	-0.75	1.30	0.28
参照样 Ref + 2.80 % SiO₂	96.67	-0.83	1.24	96.40	-0.79	1.31	0.28
参照样 Ref + 3.36 % SiO₂	96.82	-0.84	1.20	96.87	-0.78	1.59	0.40

表5：杨氏模量、断裂伸长率和最大拉伸强度
Table 5: Young Modulus, elongation at break and max tensile strength

配方 Formulation	初始值 Initial			1,000小时老化后 After 1,000h		
	硬度 Hardness	韧性 Flexibility	强度 Strength	硬度 Hardness	韧性 Flexibility	强度 Strength
	杨氏模量 Young Modulus (MPa)	断裂伸长率 Elongation at break (%)	拉伸强度 Tensile strength (MPa)	杨氏模量 Young Modulus (MPa)	断裂伸长率 Elongation at break (%)	拉伸强度 Tensile strength (MPa)
参照样 Reference (Ref)	3.6	230.56	0.89	2.80	190.59	1.10
参照样 Ref + 1.68 % SiO₂	5.1	232.18	1.26	7.67	175.31	1.50
参照样 Ref + 2.24 % SiO₂	5.9	216.52	1.31	10.22	173.62	1.66
参照样 Ref + 2.80 % SiO₂	7.0	221.27	1.37	4.24	211.64	1.38
参照样 Ref + 3.36 % SiO₂	22.0	161.14	1.63	26.59	115.73	2.04

加速老化涂料的耐沾污性 (1,000 小时)

表 9 显示耐沾污性能测试，L、a、b 和 ΔE 值。注意：添加二氧化硅时耐沾污性能的提高是持久的。

附着力

表 10 显示附着力测试数据。当使用包含硅烷改性胶体二氧化硅的组合物时，可以看到湿态和干态附着力均有改善，尤其是湿态附着力。

吸水率

表 11 显示测试三次的平均重量增加比例。测试表明，涂层的吸水性能满足要求，如 ASTM D6083 要求的最大吸水率是 20%。

水蒸气渗透性

表 12 显示渗透性。结果表明，二氧化硅的最大添加量为 2.8%，涂层的水蒸气渗透性能满足 ASTM D6083 标准不超过 50 个美制 Perms 的要求。

太阳能反射性能

表 13 显示新制备的涂层和老化后涂层的反射性能。干膜厚度约 250μm。添加胶体二氧化硅不会影响涂层的总太阳能反射率。

讨论

涂料配方稳定性和粘度降低

硅烷改性的胶态二氧化硅以其对无机颜料和填料的分散作用而闻名[20]。因此，人们非常期望当其它分散剂保持在恒定水平时，在加入二氧化硅时粘度会降低。配方稳定性的提高 (以粘度的降低表示) 很可能是由于体系具有额外的分散 / 稳定作用所致；此外，添加二氧化硅后配方中碳酸钙的量减少了 (以保持 PVC 恒定) 因此减少了系统中不稳定钙离子的数量，这也可以提供更好的稳定性。

表6：ASTM D624测试方法的抗撕裂性能测试
Table 6: Tear resistance test method ASTM D624

配方 Formulation	抗撕裂性 Tear resistance (kN m⁻¹)
参照样 Reference	12.85
参照样 Reference + 1.68 % SiO₂	17.13
参照样 Reference + 2.24 % SiO₂	17.46
参照样 Reference + 2.80 % SiO₂	19.01
参照样 Reference + 3.36 % SiO₂	18.46

表7：锥形心轴柔韧性
Table 7: Conical mandrel flexibility

配方 Formulation	ASTM D522
参照样 Reference	通过 pass 13 mm
参照样 Reference + 1.68 % SiO₂	通过 pass 13 mm
参照样 Reference + 2.24 % SiO₂	通过 pass 13 mm
参照样 Reference + 2.80 % SiO₂	通过 pass 13 mm
参照样 Reference + 3.36 % SiO₂	通过 pass 13 mm

in ambient temperatures. All tested formulations meet the requirements on low temperature flexibility.

Dirt pick-up resistance for fresh coatings

Table 8 shows the dirt pick-up resistance measurements in L, a, b and ΔE values. It can be seen, from **Table 8**, that the addition of silane modified colloidal silica reduces dirt pick-up dramatically and it is efficient towards both hydrophobic (carbon black) and hydrophilic dirt (iron oxide). (**Figure 1**).

Dirt pick-up resistance-aged coatings (1,000 hours)

Table 9 shows the dirt pick-up resistance measurements in L, a, b and ΔE values. Clearly, the enhancement of the dirt pick-up resistance upon silica addition as noted in **Table 9** is long lasting.

Adhesion

Table 10 shows the adhesion measurements. It can be seen, from **Table 10**, that improvements in wet and dry adherence, particularly wet adherence, were achieved when using compositions comprising silane modified colloidal silica.

涂层胶膜中二氧化硅的分布

评估了涂膜中 Si、Ti、Zn、Ca、C、O 的分布。将涂料在铝板上涂装约 500 微米的干膜厚度。只有 Si（即二氧化硅颗粒）显示出明显的分层，而 Ti、Zn、Ca 未显示任何分层，因为氧化锌 — 颜料，二氧化钛颜料或碳酸钙填料的分布没有变化。涂膜中的 Si（品质比）的分布如下**表 14** 中。参照样（不含二氧化硅）的 Si 含量／基线可能衍生自二氧化硅来源，例如二氧化硅表面处理的二氧化钛颜料。可以注意到加入 2.24% 和 2.80% 胶体二氧化硅的涂膜在表面出现明显富集，而添加 3.36% 胶体二氧化硅的涂膜在基材面上富集，但与参照样相比，表面上的浓度还是明显较高。细小二氧化硅颗粒的分层（非常高的小颗粒与较大颗粒比值）遵循 Keddie 等人的研究结果 [21]。

机械性能和附着力

在较高的二氧化硅负载下，硬度／杨氏模量，撕裂强度和

Water uptake

Table 11 shows the weight increase in % (average of three samples. These tests show that the water uptake properties of the coatings meet the requirements, as set out in ASTM D6083, a maximum of 20 wt-% water uptake.

Water vapour permeability

Table 12 shows the permeability in Perms. The results show that the water vapour permeation properties of the coatings with silica addition up to 2.8% meet the ASTM D6083 requirements of no more than 50 US perms.

Solar reflectance

Table 13 shows the reflectance properties of initially applied and aged coatings. It can be seen that at a dry film thickness of about 250 um, addition of colloidal silica does not affect the total solar reflectance of the coatings.

表8：耐沾污性能测试，L、a、b和ΔE值
Table 8: Dirt pick-up resistance measurements, L, a, b and ΔE values

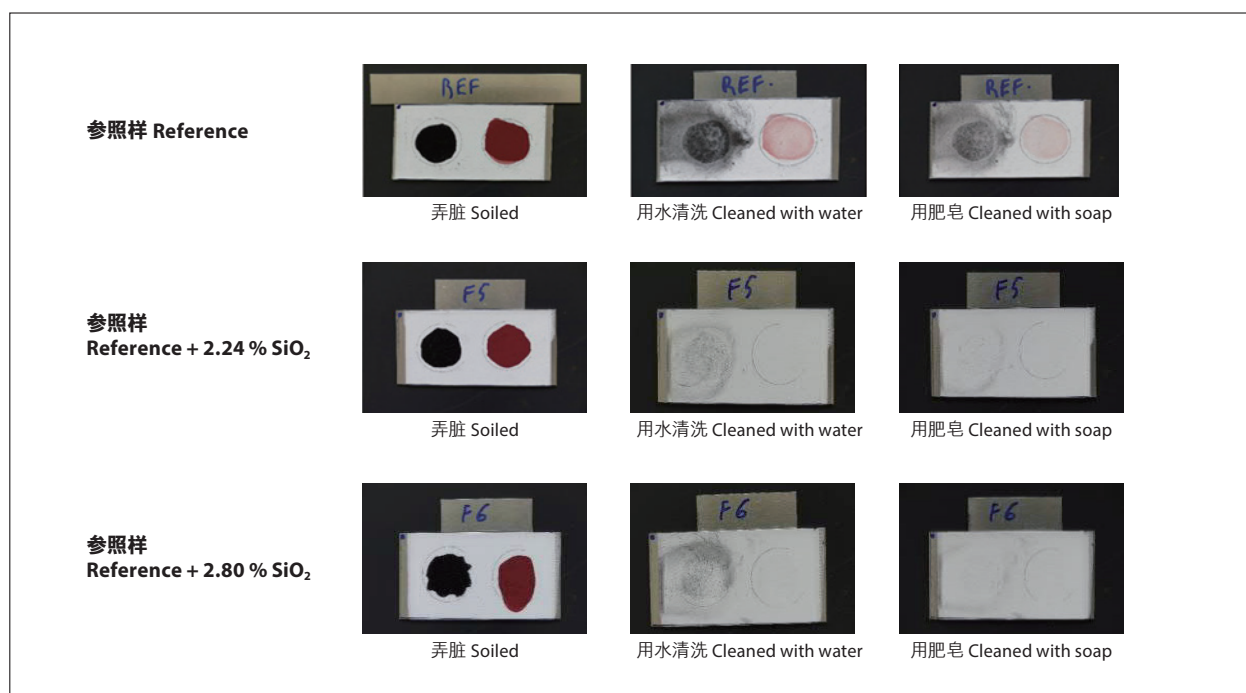| 配方 Formulation	有色– 无污染涂料 Colour – unsoiled coating			炭黑 Carbon black		氧化铁红 Red Iron oxide	
	L	a	b	ΔE - 水 water	ΔE - 肥皂 soap	ΔE - 水 water	ΔE - 肥皂 soap
参照样 Reference (Ref)	96.03	-0.69	1.93	46.83	36.87	14.14	8.10
参照样 Ref + 1.68 % SiO₂	96.52	-0.72	1.74	9.89	3.54	1.65	0.80
参照样 Ref + 2.24 % SiO₂	96.32	-0.70	1.86	10.22	1.38	0.27	0.33
参照样 Ref + 2.80 % SiO₂	96.26	=-0.71	1.86	9.38	1.42	0.78	0.17
参照样 Ref + 3.36 % SiO₂	96.62	-0.70	2.00	1.05	2.73	0.63	0.37

图1：硅烷改性胶体二氧化硅改善了疏水性和亲水性的污染物堆积。图中所列为新制备涂料上的炭黑和氧化铁。
Figure 1: Silane modified colloidal silica improves dirt pick-up resistance to hydrophobic and hydrophilic materials, exemplified by carbon black and iron oxide on fresh coatings.

表9：耐沾污性能测试，L、a、b和ΔE值
Table 9: Dirt pick-up resistance measurements, L, a, b and ΔE values

配方 Formulation	有色– 无污染涂料 Colour – unsoiled coating			炭黑 Carbon black		氧化铁红 Red Iron oxide	
	L	a	b	ΔE - 水 water	ΔE - 肥皂 soap	ΔE - 水 water	ΔE - 肥皂 soap
参照样 Reference (Ref)	96.01	-0.63	1.87	40.25	12.19	13.29	5.54
参照样 Ref + 1.68 % SiO₂	96.29	-0.64	1.66	27.89	18.35	6.50	3.78
参照样 Ref + 2.24 % SiO₂	96.46	-0.62	1.56	24.26	11.98	6.82	1.21
参照样 Ref + 2.80 % SiO₂	95.78	-0.66	1.65	21.11	8.76	10.98	3.65
参照样 Ref + 3.36 % SiO₂	96.42	-0.66	1.83	23.71	10.64	6.13	2.18

表10：附着力测试
Table 10: Adherence measurements

配方 Formulation	附著力 Adherence (干态 dry) N/m	附著力 Adherence (湿态 wet) N/m
参照样 Reference	753	256
参照样 Reference + 1.68 % SiO₂	780	500
参照样 Reference + 2.24 % SiO₂	890	879
参照样 Reference + 2.80 % SiO₂	904	842
参照样 Reference + 3.36 % SiO₂	968	948

抗拉强度的增加通常是填料效应的函数。然而，在这种情况下，二氧化硅的用量相对较低并且保持了柔韧性。可以推测，但一种解释可能是二氧化硅颗粒的表面和基材介面富集导致表面更坚固，并且可能获得一种「三明治」结构，中间部分提供了柔韧性，而表面和介面朝向基材会赋予额外的强度。撕裂强度的增强很好地遵循了增强聚合物膜的小颗粒的 Hall-Petch 理论。硅烷改性的胶态二氧化硅的最高添加量可能已开始对脆性产生某种程度的影响，并因此降低了柔韧性，如**表 5** 所示。而**表 7** 中低温柔韧性仍可以满足 ASTM D-6083 的要求。

已经发现硅烷改性胶体二氧化硅增强了用于硅酸盐涂料的混凝土基材上的附着力[17]，并且假设的功能是纳米尺寸的颗粒具有穿透基材孔隙的能力。另外，添加导致表面积增大，二氧化硅具有大量可以与基材相互作用并增强粘附性的表面基团。**表 14** 中给出的二氧化硅的分层还可以解释薄膜部分中的 Si 含量面积3 的湿态粘附的极大提高，并且遵循对湿态粘附的影响。

吸水率和水蒸气渗透性

已知胶体二氧化硅是具有完全羟基化表面的非常亲水材料，并且环氧硅烷修饰的胶体二氧化硅具有相等数量的羟基表面基，因为每个官能团与约两个硅烷醇表面基团反应，并打开环氧环，得到两个羟基[25]。由于其亲水性，可以预期吸水率和水蒸汽渗透性会略微增加。二氧化硅加入时，水蒸汽渗透性的相对增加明显高于水吸收，允许水分逸出。这可能是基于弹性体树脂的紧凑型涂膜和相对低的颜料体积浓度的效果，为水分子提供良好的阻隔性能。

耐沾污性能

硅烷改性的胶态二氧化硅以其增强疏水性和亲水性污垢抗污性能而著称[18]，特别是对于附着性得到显著改善的粘性

表11：测试三次的平均重量增加比例
Table 11: Weight increase in %, average of three samples

配方 Formulation	在水中浸入 168小时后的吸收率，（品质增加比例）Δ (%) Water uptake (weight increase) after immersion for 168 hours, in Δ (%)
参照样 Reference	Average: 11.20
参照样 Reference + 1.68 % SiO₂	Average: 12.84
参照样 Reference + 2.24 % SiO₂	Average: 14.07
参照样 Reference + 2.80 % SiO₂	Average: 15.74
参照样 Reference + 3.36 % SiO₂	Average: 15.33

Discussion

Coating formulation stability and reduction in viscosity

Silane modified colloidal silica is known for its dispersing effects for inorganic pigment and fillers[20]. It is therefore quite expected that the viscosity is reduced upon silica addition when the other dispersants are kept at constant level. The increase in formulation stability, indicated as lower increase in viscosity, is most likely a result of the additional dispersing/stabilising effect on the system. Additionally, the amount of calcium carbonate in the formulations is reduced upon silica addition (to maintain constant PVC) and hence the amount of destabilising calcium ions is reduced in the systems, that could also provide for better stability.

Distribution of silica in the coating films

Distributions of Si, Ti, Zn, Ca, C, O in the coating films were evaluated. Free films were prepared onto aluminium panels

表12：渗透性
Table 12: Permeability in Perms

配方 Formulation	公制 Metric Perms	美制 US Perms (计算值 calculated)	干膜厚度 Dry Film thickness (μm)
参照样 Reference	5.97	9.06	530.2
参照样 Reference + 1.68 % SiO₂	21.67	32.88	457.6
参照样 Reference + 2.24 % SiO₂	30.08	45.64	432.2
参照样 Reference + 2.80 % SiO₂	30.86	46.83	450.6
参照样 Reference + 3.36 % SiO₂	46.85	71.09	505.0

表13：新制备的涂层和老化后涂层的反射性能。干膜厚度约250μm
Table 13: Reflectance properties of initially applied and aged coatings (Dry film thickness about 250 μm)

配方 Formulation	太阳能总反射率 Total Solar Reflectance (%) 280-2,500nm	
	新制备涂层 Initial	老化后涂层 Aged
参照样 Reference	82.67	84.0
参照样 Reference + 1.68 % SiO₂	83.72	83.7
参照样 Reference + 2.24 % SiO₂	83.08	83.4
参照样 Reference + 2.80 % SiO₂	82.85	82.8
参照样 Reference + 3.36 % SiO₂	83.12	84.2

涂料而言 [19]。因此可以预期对污垢抗性的影响，但这种效果如**表 9** 所示，它具有惊人的强度，并且持久，即使对于在 UV 下老化 1,000 小时的薄膜，其涂膜粘性也应有所降低。较高的涂层亲水性（如上一节所述）可能是解释耐污垢性的长期效果的一个附加参数。如**表 14** 所示，胶体二氧化硅似乎需要约 5% 的二氧化硅最小表面浓度「顶面」(3.6-1.4 的 Si 等于 2.2 重量 % 的 Si，对应于 4.7 重量 % 的二氧化硅)。

涂料反射性能

硅烷改性胶体二氧化硅原则上是细小的硬玻璃颗粒，折射率为 1.470（未发布结果），接近未改性二氧化硅的 1.453 的折射率。由于其细小粒径为 7nm（基于比表面积），折射率和光散射非常低。可以期望对涂层反射率的影响是很小的，这是与研究的结果一致 (**表 13**)。

结论

在我们最近的研究中，我们已经看到硅烷改性胶体二氧化硅可以发挥关键作用，以提高丙烯酸弹性屋顶防水涂层的性能，因为这种涂层需要保持清洁以维持其性能。我们发现，对于疏水性和亲水性污染，其耐沾污性能效果持久，即使经 UV 光加速老化 1,000 小时后的丙烯酸涂层，耐沾污性能也长久。添加硅烷改性的胶体二氧化硅并未以任何负面方式影响 TSR（总太阳反射率）值，并且不会导致涂膜的任何降解。测试的起始配方符合 ASTM D-6083 中弹性体涂层的要求。

此外，屋顶防水涂层还有许多其它要求，不仅应该高度反射，而且也非常柔韧，即弹性高，并具有良好的附着力，以承受较大的温度差异和阳光暴露的恶劣条件。我们意外地发现了涂层的杨氏模量，强度和附着力得到极大提高。令人惊讶的是，还改善了涂料配方的罐内稳定性，特别是在 50℃ 的高温储存，

at about 500 microns dry film thickness. Only Si (and hence SiO₂ particles) showed significant stratification while Ti, Zn, Ca did not indicate any stratification hence no change in distribution of ZnO-pigment, TiO₂ pigment or CaCO₃ filler. The distribution of Si (as wt%) in the coating films is shown in **Table 14**. The Si-content/base-line in the reference (without silica addition) could be derived from silica sources such as e.g. silica surface treatment of TiO₂-pigment. A clear surface enrichment could be noted for the coating films with 2.24% and 2.80% addition of colloidal silica while the coating film with 3.36% showed a substrate enrichment but still a significantly higher surface concentration compared to reference. The stratification of the small silica particles (very high small particle number ratio in relation to the larger particles) follows the findings of Keddie et al [21].

Mechanical properties and adhesion

Increase in hardness/Youngs Modulus, tear and tensile strength is, at higher silica loads, often a function of filler effect. [22-24] However, in this case, the silica dosage has been relatively low and flexibility has been maintained. One can speculate but an explanation might be that surface and substrate interface enrichment of silica particles has led to a stronger surface and a kind of "sandwich" could have been obtained with a mid-section providing flexibility while the surface and the interface towards the substrate would give additional strength. The enhancement of tear strength follows the Hall-Petch theory of small particles strengthening a polymer film well. The highest addition level of silane modified colloidal silica may have started to affect the brittleness somewhat and hence reduced flexibility as indicated in **Table 5** while the demands for low temperature flexibility are still met under ASTM D-6083 (**Table 7**).

Silane modified colloidal silica has been found to enhance adhesion on concrete substrates for solsilicate paints[17] and the assumed function is that a particle of nanomateric size has

表14：通过EDS测量得到涂膜中的Si-含量, wt-%
Table 14: Si-concentration, wt-% in coating film by EDS measurement

区域 Area	参照样 Reference	Ref + 2.24 % SiO$_2$	Ref + 2.80 % SiO$_2$	Ref + 3.36 % SiO$_2$
	wt% Si	wt% Si	wt% Si	wt% Si
顶部区域 (顶部的面积) Top view (area on the top side)	1.4	4.8	5.9	3.6
区域 1 (接近表面) Area 1 (Close to surface)	1.0	2.7	4.1	3.1
区域 2 (中间层) Area 2 (middle layer)	1.0	2.7	3.7	4.3
区域 3 (接近基材) Area 3 (close to substrate)	1.0	4.0	3.0	4.7

温暖国家的仓库中很容易到达该温度。胶体二氧化硅产品的添加剂量为8至10%的范围，对应于二氧化硅的添加量为2.24至2.80%，达到最佳水平。

对自清洁性能的说明是涂层表面中二氧化硅出现明显表面富集。另外，表面和基材介面的富集可以是增强强度和表面硬度的一个原因，同时由于涂膜中间的二氧化硅浓度相对较低，形成夹层结构。

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the ability of penetrating into substrates pores. In addition, the added amount of surface area is high and the silica has a lot of surface groups that can interact with the substrate and enhance adhesion. The stratification of silica, as given in **Table 14**, could also explain the strong enhancement of the wet adhesion where the Si-content in the film section, Area 3, follows the effect on the wet adhesion well.

Water up-take and vapour permeability

Colloidal silica is known to be a very hydrophilic material with a fully hydroxylated surface and epoxy silane modified colloidal silica has equal number of hydroxyl surface groups since each functional group reacts with about two silanol surface groups and the epoxy ring is opened giving two hydroxyl groups [25]. Due to its hydrophilicity, one could expect that water adsorption would increase somewhat as well as vapour permeability, which correlates well with the findings regarding vapour permeability. The relative increase in the vapour permeability upon silica addition was significantly higher than for the water uptake, allowing for moisture to escape. That may be an effect of the compact coating film based on elastomeric resin and relatively low pigment volume concentration still giving good barrier properties for the water molecules.
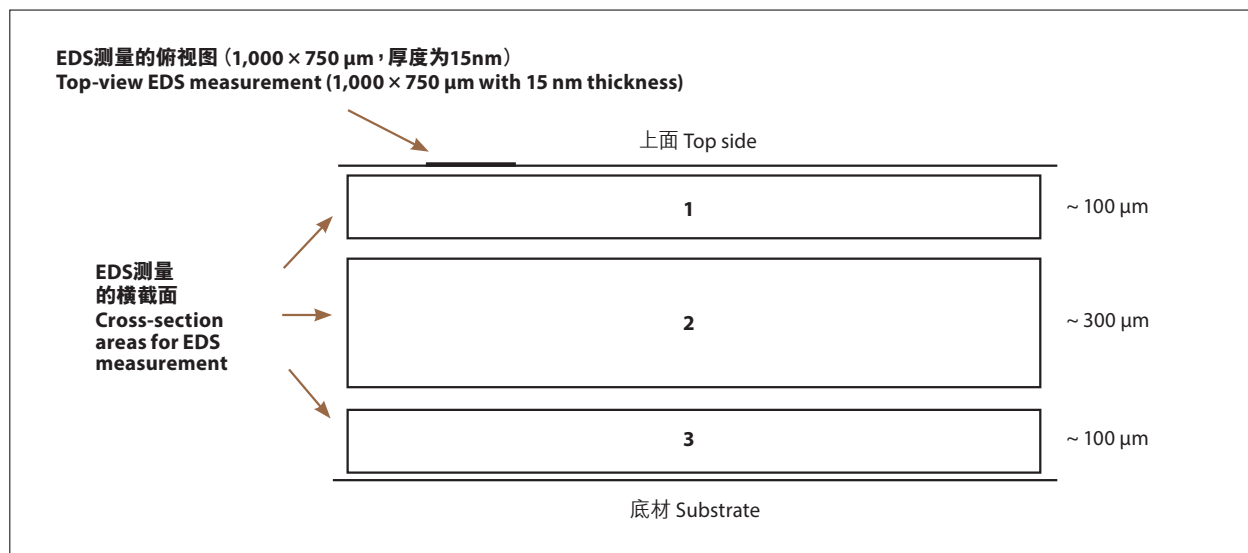

EDS测量的俯视图（1,000 × 750 µm，厚度为15nm）
Top-view EDS measurement (1,000 × 750 µm with 15 nm thickness)

上面 Top side

1 ~ 100 µm

EDS测量的横截面 Cross-section areas for EDS measurement

2 ~ 300 µm

3 ~ 100 µm

底材 Substrate

图2：EDS测量的说明。涂膜总厚度约为500µm。
Figure 2: Description of EDS measurements. Film is ~500 µm in thickness in total.

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Dirt pick-up resistance

Silane modified colloidal silica is well-known for its ability to boost dirt pick-up resistance for both hydrophobic and hydrophilic dirt [18] especially for tacky coatings where the block resistance is significantly improved [19]. The effect on dirt pick-up resistance could therefore be expected but the effect is surprisingly strong, **Table 8**, and long lasting as shown in **Table 9**, even for films aged in UV for 1,000 hours where the coating tackiness should have diminished. The somewhat higher coating hydrophilicity (as mentioned in previous section) could be one additional parameter explaining the long-lasting effect on dirt-pick up resistance. A minimum surface concentration ("top view") of approximately 5 wt-% SiO_2 as colloidal silica appears to be needed as indicated by **Table 14** (Si of 3.6-1.4 = 2.2 wt-% Si corresponding to 4.7 wt-% SiO_2).

Reflectivity of the coating

Silane modified colloidal silica is in principle small hard glass particles with a refractive index of 1.470 (unpublished results), close to that of non-modified silica of 1.453. Due to its small particle size of 7 nm (based on specific surface area), and refractive index, light scattering is very low. One could expect that the impact on coating reflectivity would be small, which is line with the findings (**Table 13**).

Conclusion

In our recent study we have seen that silane modified colloidal silica can play a key role to enhance the over-all performance of acrylic elastomeric roof coatings as such coatings need to stay clean to maintain their performance. We found a dramatic enhancement of dirt pickup resistance of the fresh coating, both for hydrophobic and hydrophilic dirt and the effect was long lasting, even after 1,000 hours of accelerated weathering of fully formulated acrylic coatings in a UV chamber. The addition of silane modified colloidal silica did not affect the TSR (total solar reflectance) value in any negative way and did not cause any degradation of the coating film. The tested starting-point formulations met the requirements as laid out in ASTM D-6083 for elastomeric coatings.

Furthermore, there are many other demands on a roof coating, not only should it be highly reflective, but also be very flexible, i.e. elastomeric, and have good adhesion to withstand big temperature differences and harsh conditions of sun exposure. We unexpectedly found a strong improvement in mechanical properties like Young's modulus, strength and adherence of the coatings without sacrificing coating flexibility for neither fresh nor aged coatings. Especially wet adhesion was significantly enhanced. Surprisingly the in-can stability of the coating formulations was also improved, especially at high temperature storage of 50°C, a temperature that easily can be reached in warehouses in warm countries. A dosage in the range of 8-10 % colloidal silica product, corresponding to 2.24 -2.80 % SiO_2, appeared to be an optimal level.

An explanation for the self-cleaning properties is the significant surface enrichment of silica in the coating surface. Additionally, the enrichment at the surface and the substrate interface could be one reason for enhanced strength and surface hardness, while maintaining flexibility thanks to relatively lower silica concentration in the middle of the coating film, giving a sandwich structure.