Source: Heiko Kverling - Fotolia

BUILDING RESISTANCE

Water-borne silicone emulsion enhances performance of organic finishes. By Ping Jiang, Louisa Maio, Vikram Kumar, Martin Wusik, Yogesh Tiwary and Mike Seeber, Momentive Performance Materials.

Silicone oils and resins can improve the weathering resistance of exterior coatings, but can have compatibility issues with water-borne systems. A new low VOC cross-linkable silicone emulsion is highly elastic with high compatibility. Good films with enhanced properties were obtained by addition to pure acrylic and styrene-acrylic emulsions and a commercial concrete paint.

Silicones have long been used to help improve the weather resistance of organic resin compositions. For example, silicone modification of alkyd and acrylic resins is used to improve their durability in solvent-borne coatings for exterior applications.

However, concerns regarding VOC emissions have prompted the development of water-based (WB) analogues. In practice, it is often difficult to introduce silicone materials into water-borne organic resin compositions due to incompatibility and immiscibility between the silicone materials and WB organic resin compositions.

Because of this, the silicone materials used as additives are typically silicone oils and silicone resins rather than cross-linked gels or elastomeric compounds. However, high additions of silicone oils and resins are often not compatible with WB organic resins.

Thus, to incorporate larger amounts of silicone materials, functional silicone intermediate materials have been used to first chemically modify organic resins, followed by emulsification. This use of silicone oils and resins requires multiple processing steps including resin synthesis and emulsification, which are not easy to practice and add cost to the final modified organic resin emulsion.

A new cross-linkable silicone emulsion ("Y-19231") has now been introduced that is compatible with WB organic resins such as acrylic emulsions. This new WB silicone is manufactured virtually free of VOCs. It cures to elastic films at room temperature, and thus achieves film properties that might typically be expected to be imparted by a cross-linked gel or elastomeric material.

Simple blending of this silicone with a WB organic resin such as acrylic emulsion produces a compatible and stable resin composition that cures to uniform films at room temperature.

KEY FEATURES OF THE NEW SILICONE EMULSION

Basically, the product is a low-viscosity emulsion of crosslinked silicone structures. Its

RESULTS AT A GLANCE

→ A new cross-linkable silicone emulsion has been developed which is highly elastic, highly compatible with standard water-borne emulsions and is almost VOC-free. Compatible films with enhanced properties were obtained across a range of additions to a pure acrylic and a styrene-acrylic emulsion.

→ In particular, "QUV" weathering performance was notably improved. Efflorescence and dirt pickup tests also showed benefits.

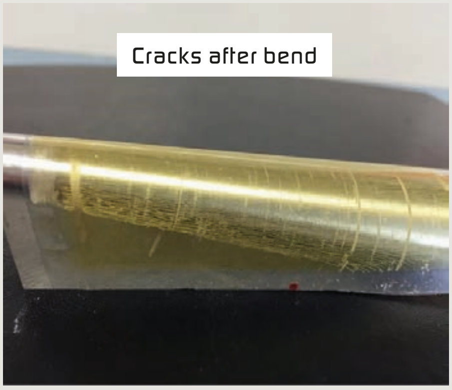
→ It was also tested as an additive to a commercial paint for concrete. Adhesion to concrete was substantially improved, both before and after heat ageing of the paints. Addition of a compatible silane further improved performance.

characteristics are summarised in *Table 1*. It can be cured to form hydrophobic elastic films at room temperature. The basic properties of cured films are also shown in *Table 1*.
For the tensile tests, film sheets were prepared from ca. 30 g silicone resin drying in a 4 x 8 inch (10 x 20 cm) "Teflon" mould at 25 °C for seven days. Elastic recovery was measured by stretching a dog-bone shaped sheet (with marked length) from 1 inch to 2 inches (2.5 to 5 cm) and holding for 24 hours at 23 °C / 50% relative humidity (RH).
The marked length was re-measured 30 minutes after releasing the tension. If the measured recovered length was the original 1 inch, then the elastic recovery was 100%.
The cured films also exhibited high temperature resistance. For example, TGA data indicated the composition of cured films was stable up to around 400 °C.
Since the silicone emulsion cures to form elastic films, it can be used as a sole binder in some coating systems. However, here the main focus is on its use as co-binder with acrylic emulsion resins. Several application examples will be presented.

ENHANCING THE PROPERTIES OF AN ACRYLIC EMULSION

The purpose of the first study was to examine the compatibility of the silicone with acrylic emulsion resin. A commercial all-acrylic emulsion for exterior applications was used as the control emulsion for comparison with various blends with the silicone emulsion. Film property comparisons are shown in *Table 2*.
The silicone was highly compatible with this commercial acrylic emulsion even at up to 30% mixing ratio. By comparison, a conventional silicone emulsion caused some incompatibility at 10% blending level, as shown by the craters observed on the co-resin film surface.
Secondly, simple blending of the silicone with acrylic emulsion increased surface hydrophobicity of the resin films. Other typical silicone properties such as lower coefficient of friction were also observed.
Micro-compositional analysis of film samples from *Table 2* can help to explain the surface properties observed. A semi-quantitative

Figure 1: Improvement in flexibility (mandrel bend test) with the addition of silicone emulsion.



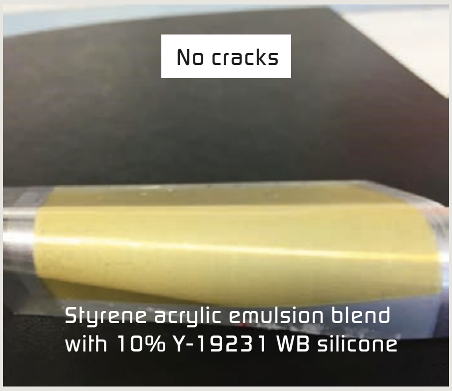


Figure 2: Efflorescence resistance is improved by the addition of silicone emulsion

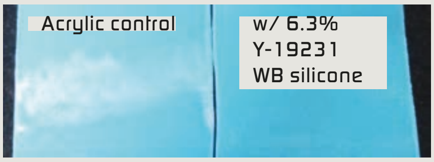


Figure 3: Comparison of dirt pickup resistance with and without silicone emulsion.

Table 1: Typical physical properties of "Y-19231" WB silicone resin and its cured films (cured at 25 °C).

Parameter	Values
Appearance	White opaque liquid
Density (gm/cm³) at 25°C	1.1
Viscosity at 25°C (mPas)	~ 20
pH value	~ 11
Cured film properties	
Tensile (psi)	~ 500
Elongation (%)	~ 450
Hardness (Shore A)	~ 30
Elastic recovery	> 90%
Tg (measured by DSC)	- 41°C

method of Energy Dispersive X-ray Spectroscopy (EDS) was used to examine the composition of resin film surfaces. EDS data indicated that there were some silicone enrichments on the blended resin film surface or near the surface (instrumental measurement depth ~ 25-200 nm).
As expected, no elemental silicon was observed from the control emulsion film. However, 6.4% of Si element by weight was observed on the 10% co-resin blend film, where 4% Si element by weight should be expected based on a theoretical calculation of uniform bulk distribution. This result indicated some silicone enrichment on or near the surface of the acrylic silicone co-resin film.

UNPIGMENTED STYRENE-ACRYLIC EMULSION IS ALSO IMPROVED

The silicone emulsion can also help improve the UV-resistance of styrene acrylic resin films. A commercial flexible styrene acrylic emulsion sample was used compared with one containing a 10% blend of the new silicone emulsion.
Both resin films were cured at room temperature on aluminium substrates and were then exposed to "QUV-B" testing for 2,000 hours. Mandrel bend testing showed the difference in flexibility of aged resin films after exposure. Cracks were seen on the control styrene acrylic resin film, while there were no such cracks observed on the co-resin film with 10% of the silicone composition added (see *Figure 1*).
Thus the silicone emulsion helped to maintain the flexibility of the resin, which would otherwise have been degraded after UV exposure.

TEST PROCEDURES FOR PIGMENTED ACRYLIC EXTERIOR PAINTS

As a co-binder in exterior paint applications, the new silicone can help to improve properties such as water resistance and UV resistance. A satin (29% PVC) and a matt formula-

Figure 4: Adhesion comparisons of "aged" paint samples with and without silicone emulsion and silane (adhesion tested over concrete).

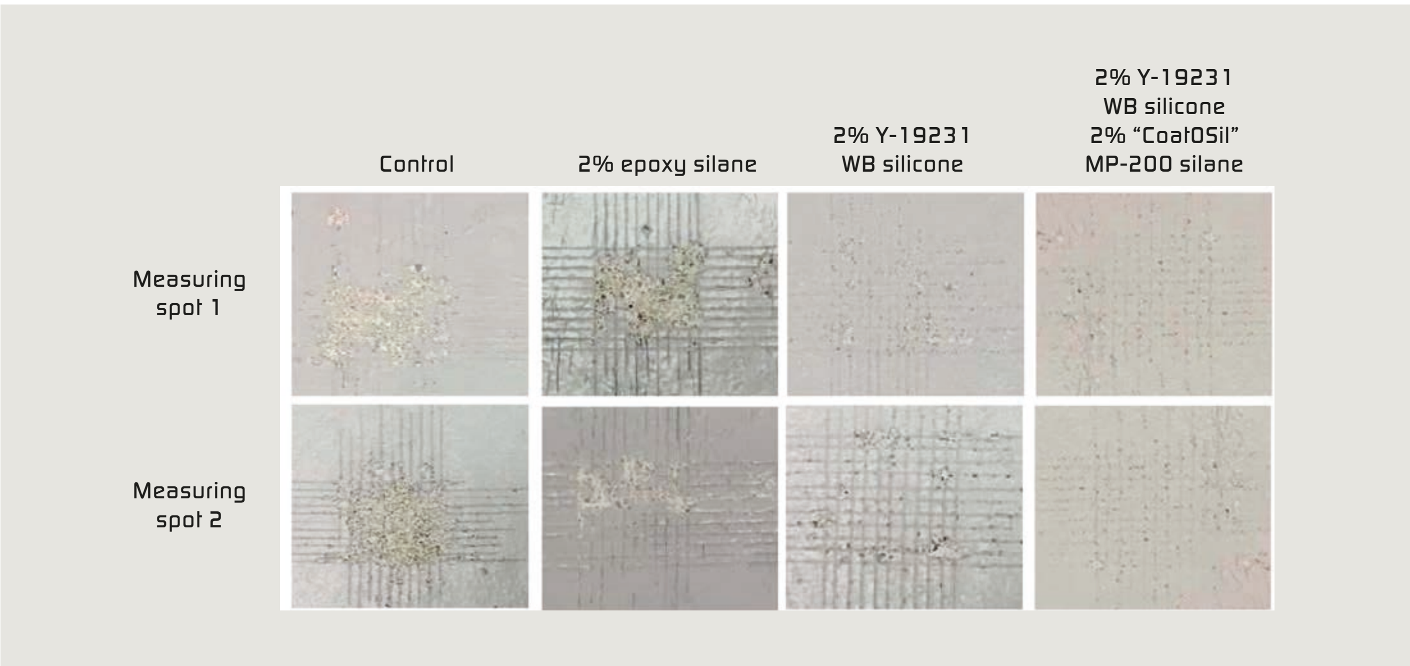


Table 2: Comparative study on blending WB silicone with acrylic emulsion as co-binder.

WB silicone level	None	10%	20%	30%	10% silicone benchmark
Compatibility & film formation	Control – uni-form smooth film	Yes – uniform smooth film	Yes – uniform smooth film	Yes – uniform smooth film	No – with craters on film
Contact angle on dry film surface	78	92	96	93	N/A
COF on dry film: static (kinetic)	0.51 (0.36)	0.28 (0.21)	0.15 (0.10)	0.13 (0.09)	N/A

tion (66% PVC) were used to demonstrate its value as a co-binder in exterior paints. Both formulations are shown in *Table 3*.

Films of the two paint samples were cured at room temperature for seven days before testing. Weathering performance by accelerated UV exposure and water absorption were tested and compared.

Accelerated weathering was done in an Atlas UV tester. Test conditions were based on ASTM D4587-11 method with 8 h UV and 4 h condensation cycles, at 0.89 W/m^2 UV intensity with fluorescent UVA lamps. A BYK "Trigloss" meter was used for gloss measurements.

Colour change (ΔE) was calculated from measured L, a, b values using a "Color Eye" spectrophotometer at different times (t) as:

$$\Delta E = \sqrt{(L_t - L_{t=0})^2 + (a_t - a_{t=0})^2 + (b_t - b_{t=0})^2}$$

An in-house water absorption test based on common industry practice was used. Free films were used for the low PVC paint after applying and peeling from Teflon tiles, but films were formed inside an aluminium pan for high PVC paints because they were too brittle to use as free films.

Films were immersed in water or water was added inside the pans and removed after 24 h and samples were weighed after draining and gently absorbing excess water with paper towel. Weight % of absorbed water was calculated as:

$(W_{final}-W_{initial})/W_{film} \times 100$

WATER ABSORPTION AND WEATHERING TESTS SHOW BENEFITS

Gloss measurements were taken of these two satin paint samples before and after UV exposure. Gloss retention for the sample with 14% silicone as co-binder was much improved over the acrylic control sample, (18% loss of gloss vs. 53% loss of gloss, respectively after 1,000 hours "QUV-A"). Colour fading of these two satin paint samples was measured after 1,000 hours of "QUV-A" exposure. The colour change (ΔE) for the acrylic blend sample with 14% of the new silicone emulsion as co-binder (ΔE = 1.8) showed a 29% improvement compared to the acrylic control sample (ΔE = 2.5).

Under the testing conditions described above, the acrylic blend sample with 14% WB silicone as co-binder reduced water absorption by 49% compared with the acrylic control sample.

Colour fading of these two matt paint samples was also obtained after 1,000 hours of "QUV-A" exposure. Colour change (ΔE) for the acrylic blend sample with 14% silicone emulsion as co-binder showed an improvement of 45% vs. the acrylic control sample (ΔE = 2.5 vs. ΔE = 4.5 respectively).

Under the same testing conditions, the acrylic blend sample with 14% of the new WB silicone as co-binder reduced water absorption by 51% relative to the acrylic control sample.

The effect of the new silicone as co-binder on efflorescence resistance in a matt paint formulation was also studied. An in-house method based on common industry practice was used (modified from ASTM D7072).

Single coats of paint with and without the silicone were applied over thin masonry (fibre cement) tiles on both faces and all sides except one. The tiles were dried at room temperature for 24 hours and then placed vertically in 2 wt% NaOH solution with the un-coated side downwards. NaOH solution migrates through the substrates from capillary action to slowly wet the painted surfaces. The tiles were monitored over several days until white salt deposits were seen on one of the samples (typically within 3-7 days), at which point the tiles were removed and dried

for at least 24 hours to visually rate the relative efflorescence resistance (see *Figure 2*).
Resistance to dirt pickup was evaluated after drying for four days at room temperature and four under exterior exposure. Stains (slurries of iron oxide or charcoal in water) were applied by paintbrush, dried for an hour at room temperature then at 50 °C for about two hours. Samples were then washed under running water while gently rubbing with a clean soft cloth. As seen in *Figure 3*, the presence of the silicone composition maintained or improved the dirt pickup resistance of the control paint.

ADHESION TO CONCRETE OF A COMMERCIAL PAINT IMPROVED

In this example a commercial 1K styrene-acrylic garage paint was used to show that the WB silicone can help improve and maintain adhesion to concrete substrates.
Paint formulations were made by post-addition of the additives to a commercially available paint based on total resin solids. The paint formulations were mixed at high speed by a mechanical stirrer for 30 min. then allowed to equilibrate at room temperature for 24 hours in a sealed container.
Concrete substrates were purchased from The Masonry Test Block Co. They were cleaned prior to application of the paint by a commercially available acidic concrete etcher and cleaner then rinsed. The substrates were allowed to dry at room temperature for 24 hours or until constant weight was observed. Paint formulations were applied by either brush or roller coating techniques. Coated substrates were normalised by total weight of dry film for each substrate. Coated substrates were allowed to cure at room temperature for a total of seven days before analysis of adhesion. Cross-hatch adhesion was measured using ASTM method D3359-09.
However, adhesion could be also quantified by counting the individual squares that remained on the concrete after four tape pulls. Sufficient adhesion between tape and concrete was ensured by using a wooden tongue depressor to press down the tape. Each tape pull was rotated by 90 degrees.
50 °C heat ageing for two weeks was performed. Paint formulations were sealed in a container and placed in an oven at 50 °C for two weeks continuously. The paint was then removed from the oven, stirred, and left at room temperature for 24 hours before coating concrete substrates. Aged paint was applied to fresh concrete substrates in the same manner as pre-aged paint formulations.
As can be seen from *Figure 4*, the adhesion performance of different 'aged' paint samples was visually compared. Due to variation in concrete surfaces, measurement was taken at two different spots. It is well known that epoxy silane can help improve the adhesion to concrete, but it often lacks the desired in-can stability, with diminishing adhesion performance during paint storage or accelerated ageing.
However when 2% of the new silicone emulsion was used as post-add additive in this paint formulation, a more robust adhesion performance before and after ageing was observed. Furthermore, a combination of "CoatOSil MP-200" silane along with the silicone showed even greater performance enhancement.

EUROPEAN COATINGS LIVE

Learn more about
water-borne silicone emulsions
at European Coatings Live
on 25 October 2016,
15.00 CET
at www.european-coatings.com/live

Table 3: Examples of satin formulation (29% PVC) and matt formulation (66% PVC), included as illustrative examples only with no representation or warranty of any kind.

Ingredient	Satin acrylic - control	Satin silicone / acrylic blend (30%/70%)	Matt acrylic - control	Matt silicone / acrylic blend (30%/70%)
Water	18.70	18.70	27.89	27.89
Dispersing agent	0.90	0.90	1.56	1.56
Non-ionic surfactant	--	--	0.11	0.11
TiO_2	17.50	17.50	10.04	10.04
$CaCO_3$	9.50	9.50	--	--
$CaCO_3$ #1	--	--	10.04	10.04
$CaCO_3$ #2	--	--	26.77	26.77
Hydroxyethyl cellulose	0.40	0.40	0.45	0.45
Amino propanol	0.20	0.20	0.22	0.22
Let-down				
Control emulsion	43.20	30.24	18.96	13.27
Y-19231 WB silicone	0.00	14.40	0.00	6.32
Non-ionic surfactant	0.10	0.10	--	--
Coalescent	1.50	1.06	0.95	0.66
Water	8.00	7.00	3.00	2.67
Total	100.0	100.0	100.0	100.0

Ping Jiang, Ph.D.
Senior chemist, silanes
Momentive
Ping.Yiang@momentive.com

"Silicone materials can also cause adhesion or recoatability issues."

3 questions to Ping Jiang

Why are there compatibility issues between silicone resins and water-borne systems? *When silicone materials are used as co-binder into water-borne systems, the issues or concerns of incompatibility can often be described by the following scenarios: not homogeneous miscible with other binders in formulation; not forming compatible co-films after cure even if miscible in formulation; silicone migration to surface(so called "silicone blooming") often seen even if compatible films appeared to have formed initially. Furthermore, silicone materials can also cause adhesion or recoatability issues. Y-19231 silicone emulsion (now commercially available as "CoatOSil" DRI water-borne silicone) was developed to address these compatibility issues.*

Which exterior applications are feasible using the new emulsions? *When used as sole binder or co-binder, Y-19231 silicone emulsion can provide the same good properties of typical silicone materials, such as good water and UV resistance, high temperature resistance etc. it also can help improve the elongation or flexibility of acrylic resins due to its durable elastic strength. So for any exterior applications where weatherability or durability is desired, Y-19231 silicone emulsion can be introduced as co-binder or sole binder in many WB formulations.*

Can the new resins also be used for indoor coatings? *Indoor coatings may have different performance requirements than exterior applications, so Y-19231 silicone emulsion may or may not be used depending on individual performance needs.*