Supporting Information

Wettability Reversal of Hydrophobic Pigment Particles Comprising Nanoscale Organosilane Shells: Concentrated Aqueous Dispersions and Corrosion-Resistant Waterborne Coatings

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Figure S1. (a) ATR-FTIR spectra of neat PMHS and K-MTHS in 4 M KOH aqueous solution, and (b) Scheme of K-MTHS synthesis from PMHS polymer via hydrolytic depolymerization in aqueous KOH.
**Figure S2.** $^{29}$Si NMR of the MeSi(OK)$_3$ dissolved in 4M KOH.

**Figure S3.** Schematic diagram demonstrates the crucial need for tight pH control during the condensation of K-MTHS on the surface of A-R-706. High pH above 9.7 leads to desorption of stabilizing amine layer and pigment aggregation. Low pH below 9.3 leads to uncontrolled K-MTHS polymerization as nanoscale polysiloxane shell on the pigment surface with negligible amine desorption.
condensation between pigment particles, also resulting in aggregation as a result of interparticle polysiloxane condensation.

**Table S1.** Effect of varying the ageing time of a wet paste of K-MTHS-A-R-706 (83 wt. % pigment and 17% water) with time required to obtain hydrophobic dry powder from a wet paste.

<table>
<thead>
<tr>
<th>No. of days of ageing</th>
<th>Day 1</th>
<th>Day 2</th>
<th>Day 3</th>
<th>Day 4</th>
<th>Day 5</th>
<th>Day 6</th>
<th>Day 7</th>
<th>Day 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying time (h)</td>
<td>10h</td>
<td>9.5h</td>
<td>8h</td>
<td>7h</td>
<td>6h</td>
<td>5h</td>
<td>5h</td>
<td>4h 40 min</td>
</tr>
</tbody>
</table>

**Table S2.** Importance of TAMOL dispersant during drying of K-MTHS-A-R-706 prior to TMS-capping.

<table>
<thead>
<tr>
<th>Material</th>
<th>Drying time</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-706</td>
<td></td>
<td>290 nm ± 5 nm</td>
</tr>
<tr>
<td>K-MTHS-A-R-706</td>
<td>0 h</td>
<td>290 nm ± 5 nm</td>
</tr>
<tr>
<td></td>
<td>7 h</td>
<td>328 nm ± 5 nm</td>
</tr>
<tr>
<td>K-MTHS-A-R-706 dried in presence of 0.6 wt. % TAMOL</td>
<td>0 h</td>
<td>290 nm ± 5 nm</td>
</tr>
<tr>
<td></td>
<td>7 h</td>
<td>290 nm ± 5 nm</td>
</tr>
<tr>
<td>TMS-K-MTHS-A-R-706</td>
<td></td>
<td>290 ± 5 nm</td>
</tr>
</tbody>
</table>
Figure S4. Schematic diagram showing the step–by–step synthesis of polysiloxane modified Ti–Pure R-706 pigment without TEA pre-treatment of Ti-Pure R-706, where ‘W’= washed, K-MTHS= Methyl trihydroxysilane tripotassium salt, ‘D’ = Dispersant, and TMS = trimethylsilyl group. Green loops having peaks and valley nature depicts the loop and tail nature of polysiloxane shell.

**STEP 1**
- (1) TAMOL™1124
- (2) 1 h stirring
- (3) Washing

**STEP 2**
- (1) Disperse with TAMOL™1124
- (2) 4 h vortex

**STEP 3**
- (1) Disperse with TAMOL™1124
- (2) Dry

**STEP 4**
- (1) $\text{H}_3\text{Si}-\text{OH}$
- (2) 24 h vortex
- (3) Centrifugation
- (4) Washing
Figure S5. DRIFT-IR spectra of 24 h dried (a) TMS–K-MTHS–A–R-706, (b) K-MTHS–A–R-706, (c) A-R-706, (d) and (e) are comparison of K-MTHS–A–R-706 before and after TMS treatment.
S1.1 Calculation of the coating volume of the condensed MeSi(OH)₃

Volume of the coating is obtained from the ratio of the weight % of the coating and the density of the coating of condensed MeSi(OH)₃:

\[
Volume \ of \ the \ coating = \frac{\text{weight} \ % \ of \ the \ coating}{\text{density} \ of \ Condensed \ MeSi(OH)₃} \quad eq \ 1
\]

Results obtained from ICP analysis showed that 2.26% coating has been grafted on the pigment surface and assuming the coating density of the condensed MeSi(OH)₃ around 1.2 g/cm³, volume of coating is calculated (using equation 1) and the value was found to be around 1.88 x 10⁻² cm³/g.

S1.2 Calculation of the surface area per gram of the pigment

For Ti-pure-R-706, particle diameter and density are 290 nm and 4 g/cm³, respectively. Using these values in equation 2, the specific surface area per gram is calculated to be 5.17 x 10⁴ cm²/g.

\[
Surface \ area = \frac{\text{surface \ area \ per \ pigment} \ (4\pi r^2)}{\text{volume \ of \ the \ pigment} \ (4/3\pi r^3) \times \text{density \ of \ the \ pigment}} \quad eq \ 2
\]

S1.3 Calculation of coverage of C/Si on the pigment surface

Coverage of C/Si on the pigment surface could be calculated from the ratio of moles of C/Si (3.4 x 10⁻⁴) on the pigment surface and external surface area per gram (5.17 x 10⁴ cm²/g; see section S1.2.):
**Figure S6.** HAADF-STEM images of (a,b) A-R-706 showing absence of bulk polysiloxane shell.

**Figure S7.** Effective viscosity and shear stress as a function of viscometer shear rate for 70 wt. % aqueous suspension of (a) K-MTHS-A-R-706 in presence of 0.3 wt. % TAMOL 1124 and (b) TMS-K-MTHS-A-R-706 in presence of 0.3 wt. % TAMOL 1124.
Table S3. Flow-behaviour index (n) from the power-law model using data in Figure 4a-f

<table>
<thead>
<tr>
<th>Material</th>
<th>Wt. % of pigment particles in aqueous slurry</th>
<th>Flow-behaviour Index (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-MTHS-A-R-706 without dispersant</td>
<td>70</td>
<td>0.62</td>
</tr>
<tr>
<td>K-MTHS with 0.05 wt. % Triton-x-100</td>
<td>70</td>
<td>0.66</td>
</tr>
<tr>
<td>TMS-K-MTHS-R-706 without dispersant</td>
<td>70</td>
<td>0.71</td>
</tr>
<tr>
<td>TMS-K-MTHS-R-706 with 0.05 wt. % Triton-x-100</td>
<td>70</td>
<td>0.60</td>
</tr>
<tr>
<td>TMS-K-MTHS-R-706 with 0.05 wt. % Triton-x-100</td>
<td>75</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Figure S8. Photograph of 60 wt. % (27.3 vol %) slurries of the TMS-K-MTHS-nonA-R-706 (a) in absence of any dispersant and in presence of (b) 0.3 wt. % TAMOL™ 1124 and (c) 0.05 wt. % TRITON X-100.
Figure S9. Effective viscosity and shear stress as a function of viscometer shear rate for A-R-706 slurry at 75 wt. % pigment contents.

Figure S10. Zeta potential versus pH for suspensions consisting of R-706, A-R-706 and TMS-K-MTHS-A-R-706 in 0.1 mM aqueous NaCl.
Figure S 11. Deconvoluted $^{29}$Si-CP/MAS NMR spectra of (a) TMS-K-MTHS-A-R-706, (b) TEA-PMHS-R-706 and (c) AMP-PMHS-R-706.
References