NOVEL APPROACHES TO IMPROVE SCRATCH AND ABRASION RESISTANCE IN UV COATINGS

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Abstract

UV Coatings have evolved to protect a broad range of substrates. One of the main performance characteristics required is excellent scratch and abrasion resistance. This ongoing search for improvement in scratch and abrasion resistance has resulted in the development of a wide variety of additive technologies to address this functionality in the marketplace. Additives chemistries differ in their physical-chem properties and in their approach to improve scratch and abrasion resistance performance.

In this study, the paper addresses a range of available additive technologies which span from surface active siloxanes and nanocomposite technology to synthetic silica and co-binders; and evaluates them side-by-side in a urethane UV curable system. The study will look at compatibility of these products in a coating formulation as well as its impact on the scratch resistance measured by several common test methods. The results will provide a comparable overview of how these various technologies perform in improving scratch resistance of the UV coating.

Introduction

As UV coatings continue to be applied to a broader range of substrates, the demand for scratch and abrasion resistance continue to grow. This is especially true with thin film applications over flexible, semi-porous or hard substrates with varying types of gloss or haptic properties. There are a variety of ways in which damage can occur due to various geometries and forces of the objects scrapping over the coating surfaces. There are many factors, such as resin composition, surface uniformity and irregularities, etc., that will influence the scratch and abrasion resistance performance of the coating. Different test methods highlight different aspects of a coating's integrity and often there is not consensus across test methods, in-regards-to, consistent performance. All these variables combined can result in a wide performance response from slight deformation which may not be visually observable to fractal failure of the polymer itself that leave visually apparent damages.

To obtain continual improvements in scratch and abrasion resistant coatings, a variety of additive technologies have been developed in the market to address this issue. In this study, the paper examines additive technologies ranging from surface active siloxanes and nanocomposite technology to synthetic amorphous silica and co-binders. These technologies are then evaluated
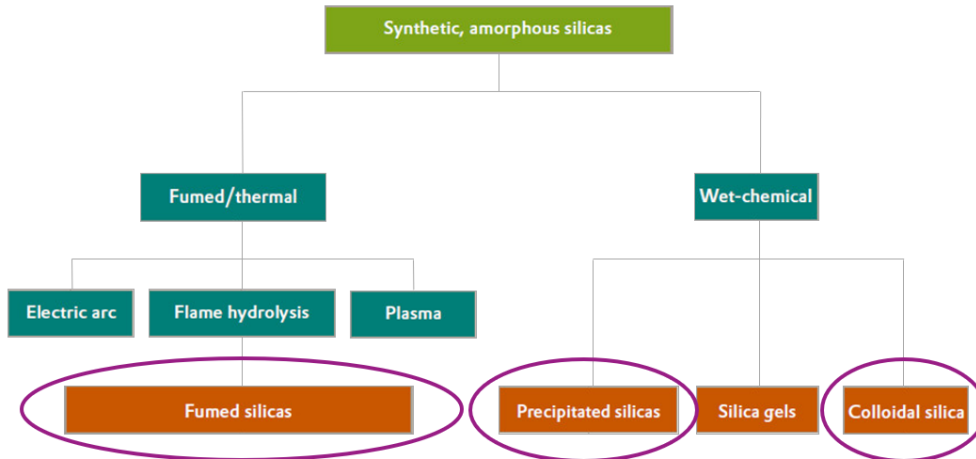
side-by-side in a urethane UV curable coating. The study will look at compatibility of these products in the coating formulation and provide relative ratings of their impact on scratch resistance. The scratch and abrasion resistance are measured using several common test methods. The results will provide a comparable overview of how these various technologies perform in improving scratch and abrasion resistance of the UV coating and the variations that can occur across testing methods.

Additive Technologies

Surface slip agents can markedly lower the damages to a coating by increasing its surface slip. These additives allow objects to slip off rather than penetrate the coating matrix. They affect the surface tension of the coating, resulting in a smoother / higher slip surface, with an improved capability to deflect force across the surface, avoiding a scratch. These additives are surface active siloxanes which exhibit weak interactions with each other and with other materials. The modified polysiloxanes migrate to the surface of the coating during cure, reducing the slip resistance of the cured film and makes it possible for solid objects scrapping across the surface to slide easier. The general structure of these additives is illustrated in Figure 1.

Figure 1. Slip agents based on polyether siloxane copolymer

These slip agents can by modified with hydrophilic-hydrophobic polyether to control its compatibility in the coating and the behavior of the polysiloxanes. Other functionalities in the chemistry of the slip agent helps with anti-cratering effects and these liquid based technologies can be formulated for varying ranges of recoatability.

Synthetic, amorphous silicas are produced with varying wet and high temperature based processes that yield similar chemical compositions but significantly different particle types and morphologies, with a wide range of physical-chemical properties. The three types of silica used in this study are shown relative to the overall synthetic amorphous silica market in Figure 2. Fumed silica is derived from a high temperature process. Whereas, both precipitated and colloidal silica are derived from a wet process.

Figure 2. Types of synthetic, amorphous silica

A typical function for most amorphous silica is to improve the overall hardness and reinforcement of the coating. Structure modified fumed silica is manufactured using the high temperature flame hydrolysis that produces primary particles which are irreversibly fused to form sub-micron aggregates. These aggregates are then processed to form structure-modified particles. The wet process produces precipitated and colloidal silica. The precipitated silica is a unique spherical particle which differs from conventional precipitated silica. The colloidal silica is functionalized to provide better compatibility in coating formulations while maintaining excellent dispersion stability in water. The colloidal silica in water is designated nanocomposites in this study.

Fumed silica - TEM photos in Image 1 shows the conventional structure of fumed silica on the left and the structure-modified fumed silica on the right. This silica has higher bulk density and more compact structure, allowing for higher loading level without adversely affecting viscosity.
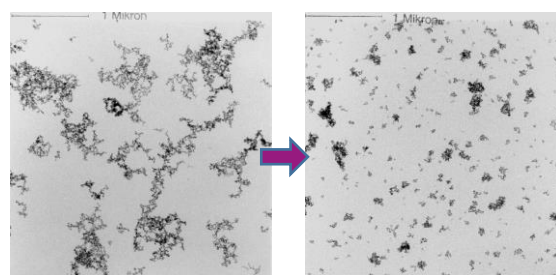
Image 1. Conventional vs structure- modified fumed silica

Precipitated silica – In Image 2 on the following page, a novel new spherical precipitated silica is shown in the center surrounded by TEM images of other conventional precipitated silica as well as other similar products on the market such as natural ground silica, diatomaceous silica and synthetic microspheres. The particle porosity and sphericity of the new novel precipitated silica

is controlled by the manufacturing process, resulting in linseed oil absorption of 40ml/100g silica and BET surface area of < 15m^2/g.
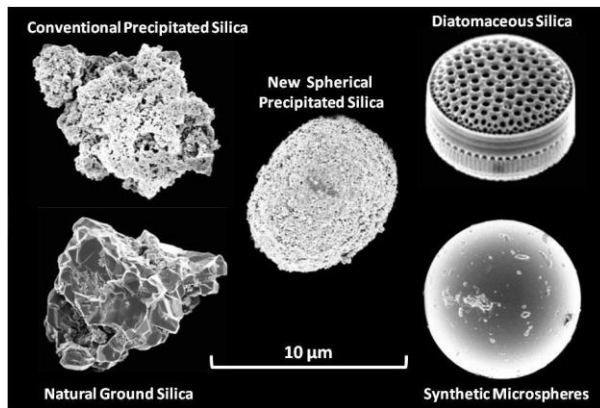

Image 2. TEM of precipitated and natural silica

The nanocomposites are aqueous dispersions of colloidal silica. Like the fumed and precipitated silica, the colloidal silica improves the overall hardness of the coating while providing improved mechanical properties among other attributes and due to its very small size achieves very high clarity.   Image 3 is an example of a mono-dispersed, discrete silica nano-particles of 20 nm distributed uniformly throughout a cured film.   These particles are functionalized and stabilized in the aqueous dispersion. For UV curable systems, dispersions in various monomers are also available. Particle based dispersions in solvent and water are also available.
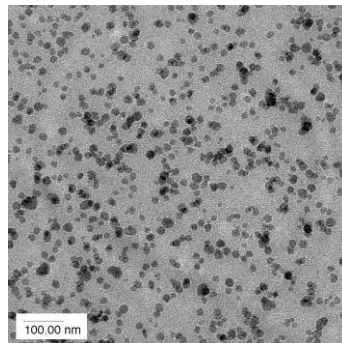
Image 3. TEM of colloidal nano-silica in cured sample.

The last group of property enhancers are co-binders that can improve the overall hardness of the coating by increasing the overall glass transition temperature (Tg) when combined with the main resins in the final coating. Here, two co-binders are included – a high Tg polyester and high Tg Keton-resins, shown below in Figure 3 on the next page.
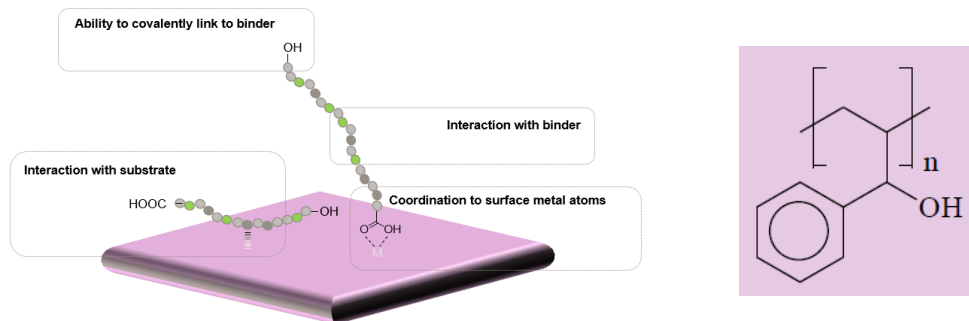
Figure 3. High Tg polyester and Keton resins

The Tg of both the polyester and Keton-resin co-binders are at 90°C.

Test Formulation

Test formulation is shown in Table 1. The additives were added at 0.1-10.0% on formulation. The silica content was added at 10.0% above the total formulation.

Raw Material Description	Amount
Aliphatic urethane acrylate (EBECRYL® 5129)	30
Reactive diluent A (TPGDA, difunctional)	33
Reactive diluent B (TMPEOTA, trifunctional)	20
Additives	0.1-10.0%
Levelling agent (TEGO® RAD 2100)	0.6
Photoinitiator A (GENOCURE® MBF)	2.2
Photoinitiator B (Omnirad® 1173)	2.2
Isopropyl alcohol	2
Total	110
SiO_2 - % on top of formulation	10

Table 1. UV coating test formulation

Sample Preparations

Wet samples were prepared by weighing 100 grams of test formulation into a beaker, then incorporating various levels of the additives, then mixing for 3 minutes at 1000 rpm using a 30 mm diameter dissolver blade. These samples were then applied on different substrates and cured using UV-Light at a speed of 20m/min.

Testing Methods

The scratch and abrasion resistance were tested using various methods listed in Table 2 on the following page.

Test Method	Application	Analysis
Martens Hardness	• Substrate: Glass • Bird bar 100 µm • Curing: 2 cycles in a UV-oven	Martens hardness (HM) [N/mm²]
Martindale Tester (testing as per VW standard PV 3975)	• Substrate: System Leneta®-black foil • Wire bar 100 µm • Curing: 2 cycles in a UV-oven	• Visual assessment of the surface for compatibility • Determination of gloss value [GV], angle of measurement 20°, after stress (50 cycles/3M polishing paper-grade 9MIC) and after 7 days RT (reflow) The abrasion resistance is given as residual gloss in % $\text{Residual gloss in \%} = \dfrac{\text{Gloss level after the test} \times 100}{\text{Gloss level before the test}}$ The surfaces of the various components are divided into three requirement areas. A = > 85 % residual gloss / high abrasion resistance B = 85 to 40 % residual gloss / medium abrasion resistance C = < 40 % residual gloss / low abrasion resistance
Crockmeter Tester	• Substrate: Acrylonitrile butadiene styrene (ABS)- black sheet • Wire bar 100 µm • Curing: 2 cycles in a UV-oven	• Visual assessment of the surface for compatibility • Determination of gloss value [GV], angle of measurement 20° & 60° after stress (10 cycles/3M polishing paper-grade 9MIC) The abrasion resistance is given as residual gloss in % $\text{Residual gloss in \%} = \dfrac{\text{Gloss level after the test} \times 100}{\text{Gloss level before the test}}$
TABER® Shear/Scratch Tester 551	• Substrate: Acrylonitrile butadiene styrene (ABS)- black sheet • Wire bar 100 µm • Curing: 2 cycles in a UV-oven	• Conical Diamond Tool (Models 139-55) • Load in grams until the destruction of the paint film (up to the substrate)
TABER® Abraser Tester	• Substrate: Acrylonitrile butadiene styrene (ABS)- black sheet • Wire bar 200 µm • Curing: 2 cycles in a UV-oven	• Weight loss after 500 r[mg] CS-10

Table 2. Scratch/Abrasion test methods

Results and Discussions

The additives from each of the technology areas chosen for this study are listed in Table 3 on the next page. When the additives are added and mixed into the formulation, its compatibility to the system is checked.

Additive	Description
Slip Agents	
Slip 410	Polyether siloxane copolymer, 100% Active
Slip 432	Polyether siloxane copolymer, 100% Active
Slip 496	Polyether siloxane copolymer, 100% Active
Slip 500	Silicone acrylate, 100% Active
Silica	
PPT Silica	Spherical precipitated silica
SMF Silica	Structure modified fumed silica
Nanocomposite	
NC 153	Nano silica particles in water, 43 % solids
NC 650	Nano silica particles in water, 31 % solids
NC 652	Nano silica particles in water, 31 % solids
Cobinder	
CB LTH	Polyester resin, Tg = 90°C
CB SK	Keton resin, Tg = 90°C

Table 3. Additives evaluated in this study

Some of the additives were incompatible and flocculated in the beaker after a short time. Others showed incompatibility at lower concentrations but incorporated uniformly at higher concentrations. Finally, some resulted in an inflexible film at higher concentrations that cracked and could not be used for testing. Some examples of these are shown in Image 4 below.

Image 4. Examples of incompatibility at lower concentration and inflexible film at higher concentration

The formulation for this study was not fully optimized to take into consideration some of the incompatibility or concentration effects. Summary of the test results are listed in Table 4.

	Dosage [%]	Compatibility	Martenshardness MH [N/mm²]	Abrasion Test Gloss GV 20°	Martindale Residual [%] Gloss GV 20°	Crockmeter Residual [%] Gloss GV 60°	Shear Test (g)	TABER® Abrader Test CS-10 loss after 500 r [mg]
Blank		1	93.8	71.0	66.9	78.8	1.7	20.5
Slip 410	0.1	2	96.7	74.0	72.0	81.0	3.0	26.5
	0.5	2	95.4	81.4	74.2	82.6	3.7	16.5
Slip 432	0.1	2	86.2	74.4	75.7	83.8	3.0	27.5
	0.5	2	76.5	76.8	71.1	80.5	3.0	26.0
Slip 496	0.1	2	99.3	71.9	78.2	85.8	2.3	17.0
	0.5	2	95.4	78.5	74.7	83.0	2.9	18.0
Slip 500	0.1	5	------	40.2	19.3	54.7	------	47.0
	0.5	2	76.5	74.2	74.1	84.5	2.5	47.0
PPT Silica	3.0	2	88.6	61.4	73.5	83.5	2.0	31.0
	5.0	2	93.1	61.5	60.6	75.5	1.8	35.0
	10.0	3	------	43.9	48.4	73.3	2.1	19.5
SMF Silica	3.0	6	Incompatible (sample flocculated in the UV-system)					
	5.0	6						
	10.0	6						
NC 153	3.0	2	80.5	71.1	76.8	86.0	2.3	13.0
	5.0	2	80.8	73.3	76.9	85.7	2.2	17.0
	10.0	2	87.7	72.0	79.5	86.6	2.4	18.0
NC 650	3.0	2	57.9	70.1	79.5	86.4	1.0	------
	5.0	3	------	62.1	80.7	87.4	------	------
	10.0	5	------	------	59.2	73.5	------	------
NC 652	3.0	2	56.5	64.7	74.3	83.5	1.5	------
	5.0	3	54.9	61.8	74.1	83.8	------	------
	10.0	5	------	------	64.0	80.5	------	------
CB LTH	3.0	2	68.0	63.2	65.1	76.9	2.3	24.0
	5.0	2	58.6	72.4	65.3	77.6	1.5	29.5
	10.0	2	41.4	74.0	63.4	76.3	1.4	25.0
CB SK	3.0	2	66.0	75.3	63.3	74.1	1.9	23.0
	5.0	2	51.7	76.8	58.0	73.0	1.6	28.0
	10.0	2	42.0	76.3	67.0	79.0	1.7	20.5

**Table 4. Summary of test results**

In general, the slip additives and co-binders had good compatibility with the exception of Slip 500 at lower concentrations. The slip additives are surface active agents, therefore only low dosages are needed. The structure modified fumed silica (SMF Silica) showed incompatibility due to the need to grind these particles in a high energy mill and pre-stabilized before addition into a coating formulation. Therefore, we were unable to obtain any results with this material in this study. Finally, the nanocomposites, at higher concentrations some of these property enhancers resulted in inflexible films which could not be used in measuring its scratch and abrasion resistance.

Since the structure modified fumed silica (SMF Silica) was incompatible, they are left out in the following analysis. The remaining blanks in the graphs are because the measurements could not be obtained from the coating applied.
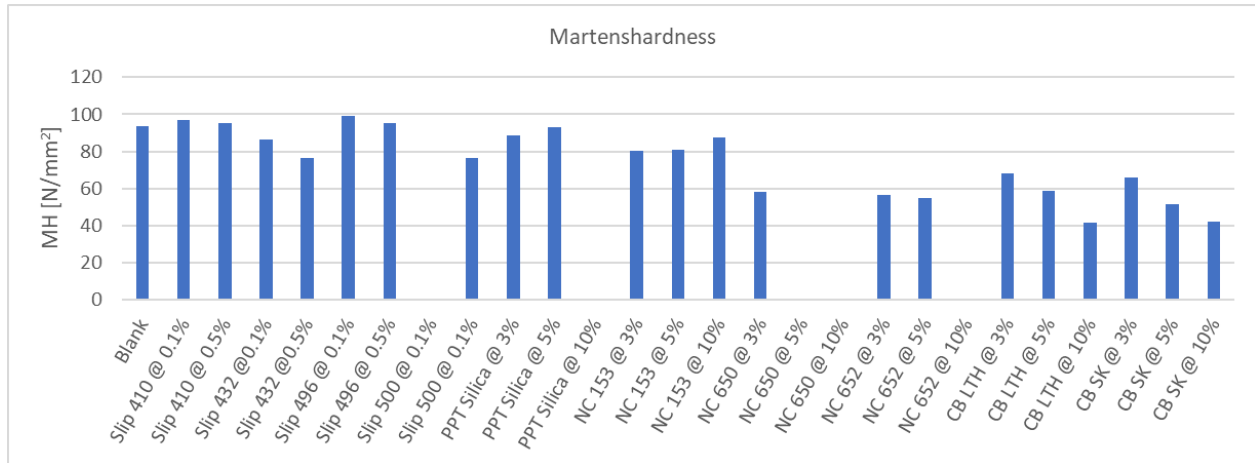

Graph 1. Martens Hardness MH

Martens hardness in Graph 1 shows that some additives can reduce the hardness of the coating. This was especially true of the co-binders. The nanocomposites did not form films that were acceptable for measurements except for the NC 153. However, even this reduced the MH of the coating. Here, the best performance was seen with the Slip 496 where at 0.1%, results were better than the blank coating itself.
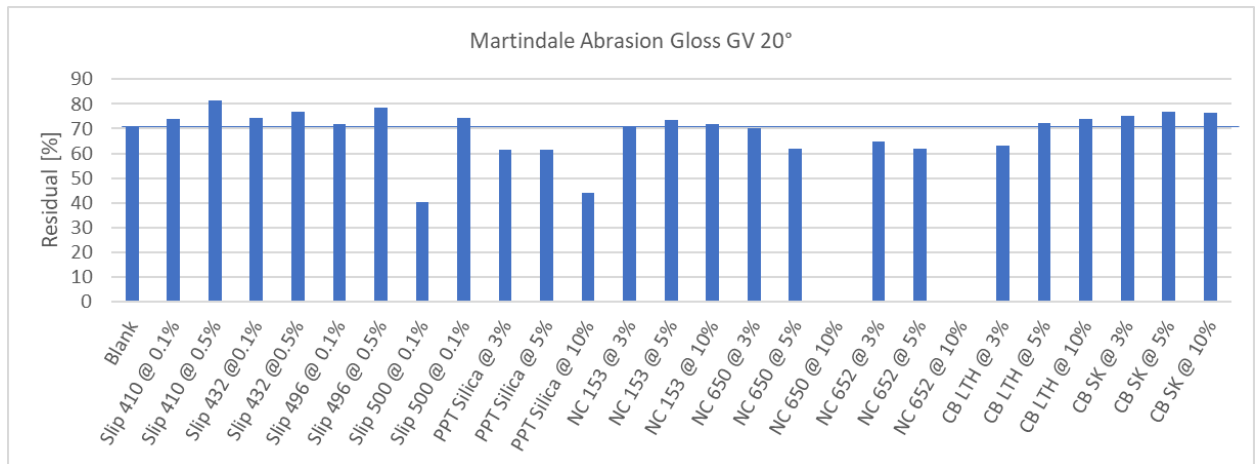
Graph 2. Martindale Abrasion at Gloss GV 20°

The Martindale abrasion test also showed the best performance was with the slip agents where both the Slip 410 and 496 both performed well. Here the co-binders gave good performance at the higher loading levels. Of the nanocomposites, the NC 153 had more consistent performance.
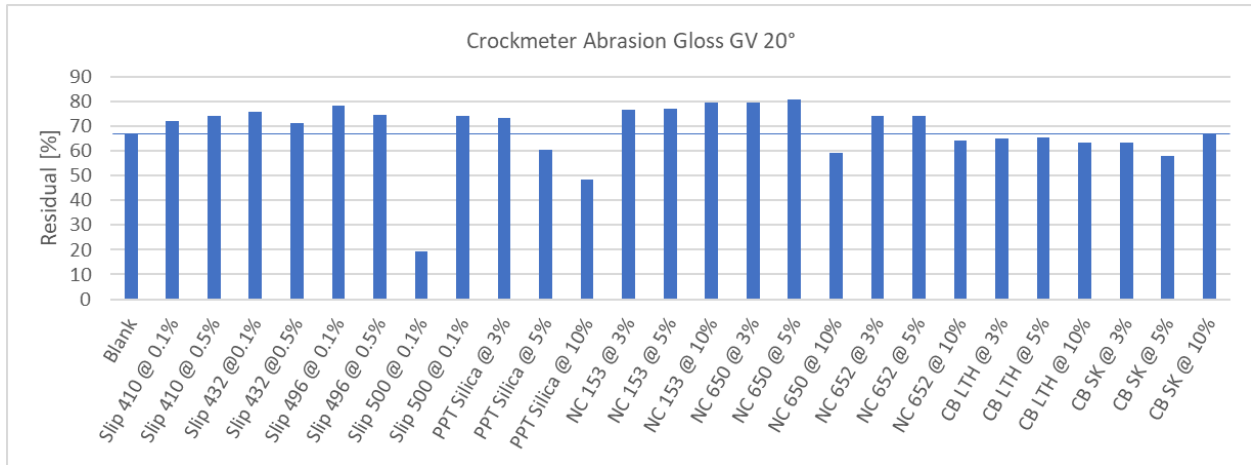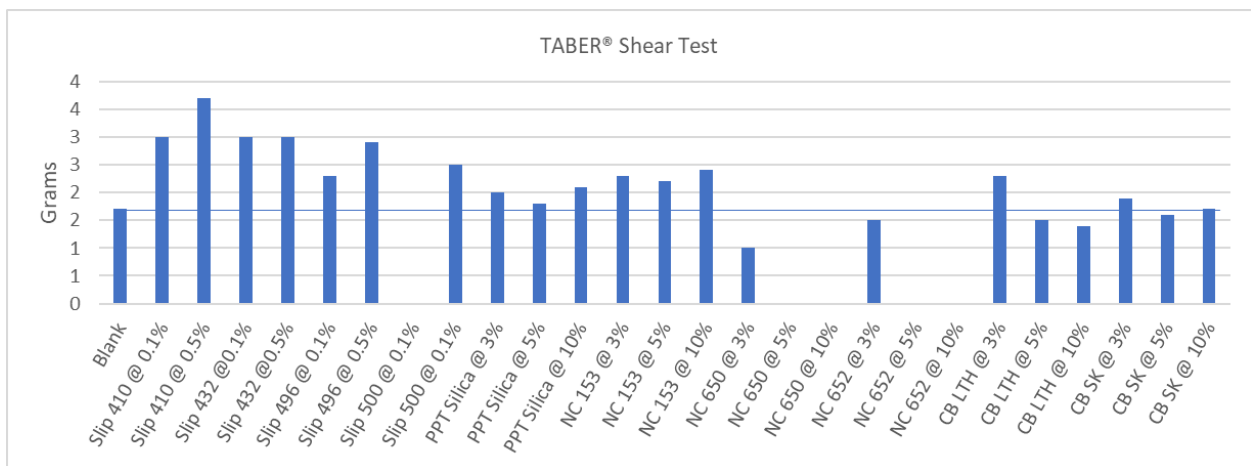
**Graph 3. Crockmeter Abrasion at Gloss GV 20°**
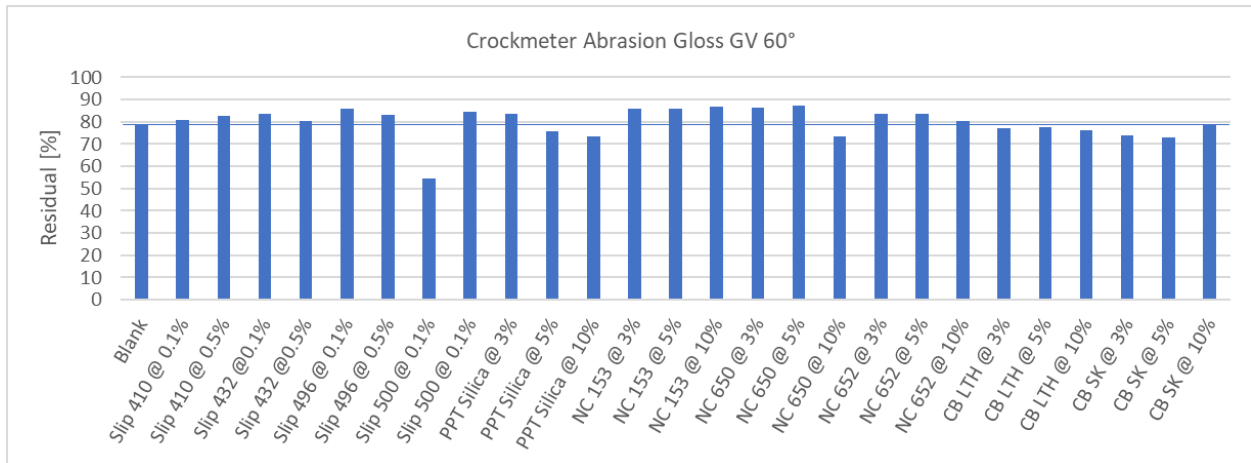
Graph 4. Crockmeter Abrasion at Gloss GV 60°

When we look at the Crockmeter abrasion results at both Gloss GV 20° and 60° in Graphs 3 and 4, the nanocomposites showed best performance followed closely with Slip 496.


Graph 5. TABER® Shear Test

In the TABER® Shear test shown in Graph 5 on the previous page, the slip agents allow for higher weight on the shear arm before it begins to scratch the coating. Here, the best performance is shown with the slip agents, specifically the Slip 410 providing the best performance. Among the nanocomposites, the NC 153 had the best performance.
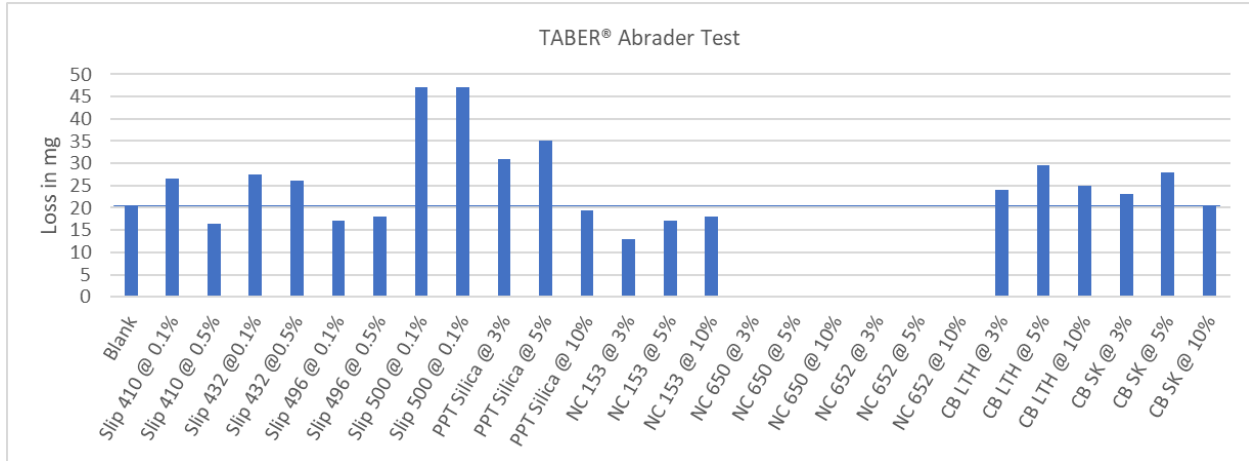
Graph 6. TABER® Abrader Test

Finally, when the additive's impact is evaluated using the TABER® Abrader test, the best performance is between the Slip 496 and the nanocomposite NC 153.

If we consider lowest dosage for slip additives, due to their surface activity and highest dosage for the silica and nanocomposites, their impact on the coating can be summarized in Graph 7.
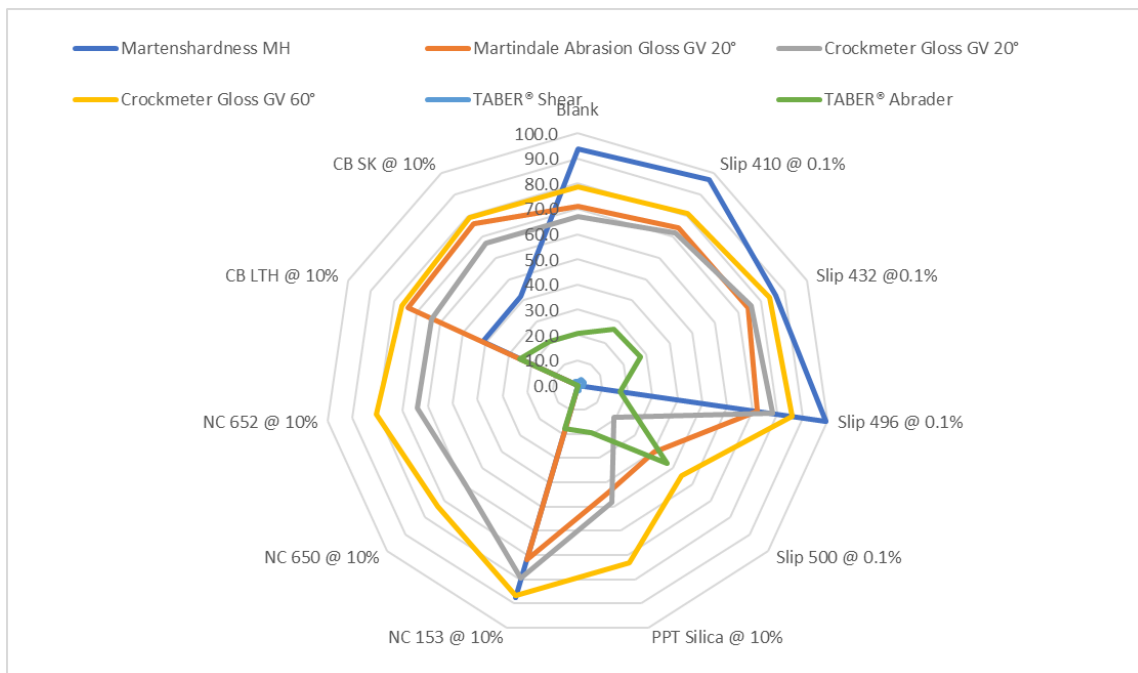
Graph 7. Summary of additives performance

From these results, the slip additives generally performed best across these tests in this UV curable coating formulation. The Slip 496 was the best performer among the slip additives. Following the slip additives is the nanocomposite technology, of which the NC 153 offered the best performance.

As stated, this study was to provide an overview of the comparable technologies. However, further developments would be necessary to optimize formulation and incorporation of the various technologies to provide definitive results on performance.

Conclusions

The study provides an overview of comparable technologies to improve scratch and abrasion of UV curable coatings. The results showed that slip additives perform best in this study with the Slip 496 giving the best overall performance. Following the slip additives would be the nanocomposites, of which NC 153 had the best performance.

This study also demonstrates that scratch resistance performance can vary significantly depending on which method is used and often there is not a common improved performance across each and every scratch test.

Further work would be needed to examine the incorporation of additives such as the novel precipitated spherical silica, or the structure modified fumed silica. In addition, there is a need to optimize nanocomposites to obtain best compatibility and performance.

Acknowledgement

References

1. Evonik Report PLO2018-03 - Scratch-Resistance UV-System by Mr. Reinartz and Ms. Skotarczak.
2. "Testing of Scratch and Abrasion Resistance of Coating Systems for Permanent Protection of Plastics and Other Substrates" by M. Heuer, A. Skotarczak, M. Schaepermeier, R. Reinartz, and F. Eichenberger; presented January 2020.