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Inside: Construction Coatings

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Protecting the planet

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Dr Meinhart Roth, *Susanne Reiter* and *Hubert Oggermüller*, Hoffmann Mineral GmbH, discuss how the use of NSE in road marking paints can reduce costs and improve performance

Neuburg Siliceous Earth as a functional extender for high performance road marking paints

Public roads without sufficient road markings, especially roads carrying high traffic volumes, would lead to an outstanding amount of accidents and would, therefore, drastically reduce our individual mobility[1]. International statistics and investigations, give clear evidence that especially in Africa and south east Asia (SEA), the amount of traffic fatalities is increasing every year and that also road markings have a substantial impact on traffic safety aspects, especially under night driving conditions[2,3].

When creating a modern road marking paint, many things have to be considered, starting with legislative regulations, environmental restrictions, infrastructure, climatic conditions and obviously the all over formulation costs, which challenges developers all over the world to create a state-of-the-art solution.

In past decades, different types of road marking technologies have been established in the market, which can be subdivided into solvent-based, water-based and thermoplastic systems. Nowadays, the most common products are water-based formulations as a logical consequence of the worldwide efforts to reduce the amount of VOC's. Thermoplastic formulations have a considerable market share especially in SEA, attributed to the harsh climatic conditions including high temperatures and heavy rain during monsoon season[4].

The most common thermoplastic binder is C5 resin. It is usually based on a mixture of various hydrocarbon monomers, which allow an adjustment of the glass transition temperature (T_g). The T_g is the most critical property of hot melt thermoplastic resins due to its decisive impact on the softening point of the resin. It plays a crucial role for the processing and the final durability of the coating. If the softening point is too low it can lead to a weak performance under outstanding hot conditions, whereas crack formation is expectable under cold conditions for resins with a high softening point. This fact might also explain why the use of C5 resin in colder countries is not so common, although special grades are available nowadays that exhibit higher flexibility towards low temperatures[5,6].

Another important fact, which must be respected, is the complexibility of the formulations when you compare water-based and thermoplastic systems. Usually the hot melt thermoplastic types are straightforward mixtures of C5 binder, plasticiser, fillers and reflective pearls, whereas water-based systems are multicomponent formulations utilising various additives and modifiers to guarantee accurate storage stability, good spray ability and obviously acceptable mechanical durability.

Summarising the mentioned points, water-based systems exhibit higher flexibility because they also allow for complex geometries combined with a neglectable impact of the road surface smoothness within a broad spectrum of temperatures, in contrast to their thermoplastic counter parts[7]. Thermoplastic systems result in thick, durable markings, which require less effort in the development and exhibit a superiority in terms of raw material costs compared to modern water-based formulations.

Besides the previously mentioned issues, both types of coatings contain high dosages of filler to keep the price low and to optimise the mechanical stability of the final films. Here, the standard raw material is calcium carbonate due to its unique low price and good availability, although it usually has a negative effect on the formulation's performance. This deterioration is a result of the low mineral hardness of the calcium carbonate, the tendency to absorb high dosages of water and the limited chemical stability.

To compensate for these negative aspects of calcium carbonate, we want to introduce in the present article the use of Neuburg Siliceous Earth (NSE) for water-based and C5 resin-based road marking paints. This paper will outline opportunities to improve performance and reduce the overall formulation cost at the same time by the partial replacement of TiO_2 and yellow pigments with Hoffmann's functional fillers.

Due to the unique mineralogical morphology of NSE, which is a natural combination of corpuscular Neuburg Silica and lamellar kaolinite, outstanding results can be obtained that pave the way towards novel high performance and economically feasible road marking paint formulations.

RESULTS AND DISCUSSION:

As was already mentioned in the introduction, we want to demonstrate in the present study the use of two different Hoffmann Mineral products for water-based and C5 based road markings.

In particular we focused on the grades Sillitin N 82 and Silfit Z 91.

Sillitin is the trade name for standard Neuburg Siliceous Earth products. All different grades of Sillitin are labelled with a letter (V, N, Z, P) and number (82-89), which are representative of the particle size and the colour of the natural occurring mineral.

Silfit is the calcined grade of the NSE, which exhibits outstanding brightness, colour neutrality, low water uptake and excellent chemical stability.

Attributed to the fact that most road marking paints are yellow or white, depending on the country and application, the above mentioned products are the perfect candidates to add further value to various formulations. Sillitin N 82 exhibits

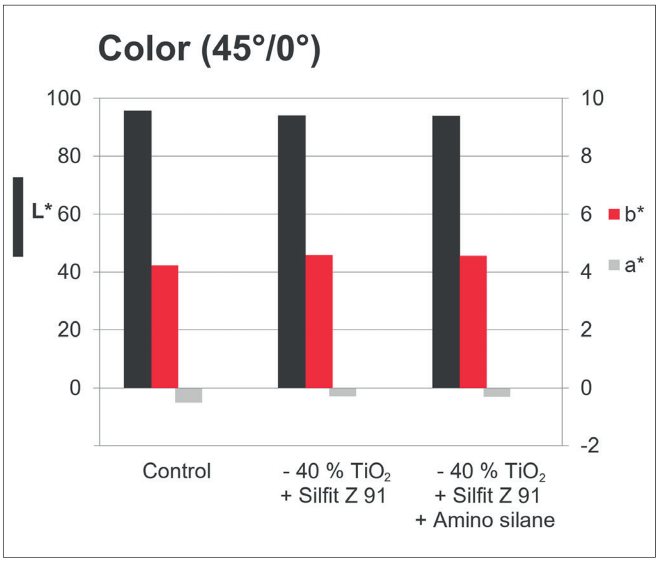

Figure 1. Colour ratio after partial TiO_2 replacement at a wet film thickness (WFT) of 600µm

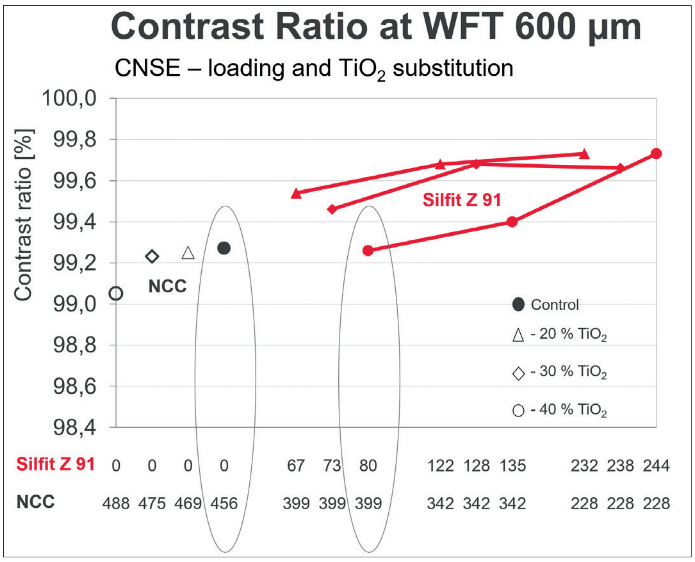

Figure 2. Contrast ratio after partial TiO_2 replacement at a WFT of 600µm

a natural yellowness, attributed to a certain amount of iron containing minerals naturally accompanying the unique mixture of corpuscular Neuburg Silica and kaolinite[8]. This special and also specified colouration enables a partial replacement of the yellow pigment in the road marking paint, improving the overall formulation costs. Furthermore, the filler is very easy to disperse in the formulation due to its unique morphology and small particle size. The dosage of Neuburg Silica, which is the main component of the material (approx 70%), also increases the final hardness and abrasion resistance of the applied film.

Similar properties can be found in white formulations when Silfit Z 91 is used as a TiO_2 extender. In contrast to most of the regularly used extender materials on the market, a significant improvement of the abrasion resistance can also be observed as a logical result of the higher mineral hardness compared to other extenders, such as calcined clay, calcium carbonate, talc and others.

System 1: Water-based road marking paint

To illustrate the performance of NSE in water-based road markings, a representative formulation was developed based on an acrylic dispersion **(Table 1)**. This formulation contained a high dosage of calcium carbonate and 9.6% of TiO_2, which was partially replaced by Silfit Z 91. To obtain the best possible results 12.5pbw calcium carbonate was also replaced at equal volume beside the replacement of 40% TiO_2. The PVC was kept on a constant value of 51%.

Here, the low impact on the optical impression of the paint when TiO_2 is partially replaced by Silfit Z 91 **(Figures 1 and 2)** and the improvement of the mechanical performance **(Figure 3)** was observed, as well as in comparison with a formulation that was further tuned by the addition of amino silane to optimise the abrasion resistance.

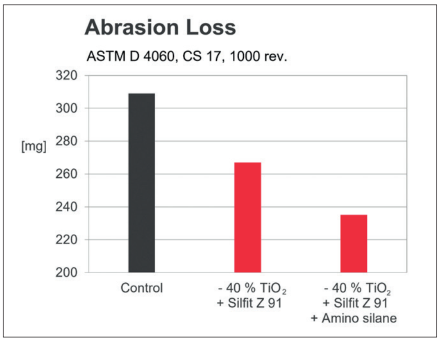

Figure 3. Abrasion resistance after partial TiO_2 replacement with Silfit Z 91 pure and Silfit Z 91 + amino silane

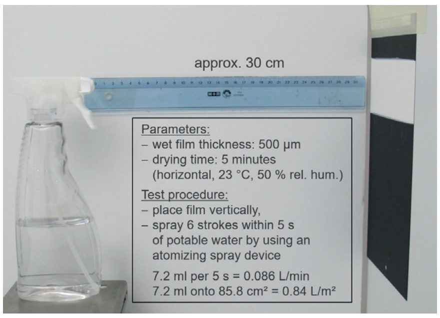

Figure 4. Testing set-up for the early rain resistance measurement

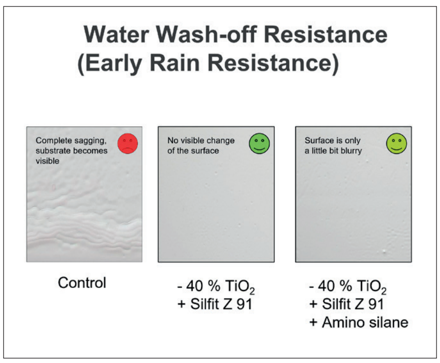

Figure 5. Results after early rain exposure of the evaluated road marking formulations

Besides optical and mechanical properties, it is also worth mentioning that the drying time and subsequently the early rain resistance can be positively influenced by the described formulation optimisation.

Drying behaviour is dependent on the surrounding temperature, the humidity of the air and the applied film thickness. The lower the temperature, the higher the relative humidity and the larger quantity of marking colour applied, the more time the drying will take. This can lead to problems during critical seasons with high amounts of precipitations. If a marking paint that has not yet dried completely is exposed to rainfall, it will frequently run off as it has not yet attained the required water resistance, ie, it is not yet “rain proof”.

The expression “Early Rain Resistance” was chosen to indicate the drying behaviour of road marking paints, which ideally even under unfavourable weather conditions should rapidly become “rain proof”.

The test was carried out based on ASTM D7538. With the aid of a doctor blade (gap height 500µm, film width 6cm), the road marking paint was applied to a Leneta film. After drying for 5min in horizontal position at 23°C and 50% relative air humidity, the Leneta film was attached vertically to a wall.

Using a Trigger Sprayer, the marking paint was sprayed on from a distance of 30cm within 5sec with 6 shots of tab water (this corresponds to 0.086l/min or 0.84l/m^2). The Leneta film was then taken off the wall immediately and dried in a horizontal position at room temperature **(Figure 4)**.

The assessment of the "Early Rain Resistance" was done on the dry film. The road marking surface was assessed optically **(Figure 5)** and the superiority of the modified formulations after the artificial early rain exposure could be observed at first sight.

System 2: C5 thermoplastic road marking formulation

The second system was a model formulation for a thermoplastic C5 based road marking where the partial replacement of TiO_2 and yellow pigment were shown. The main focus was on the raw material cost reduction for both formulations and to keep the mechanical performance at least at a constant value. Due to the cost driven approach, the dosage of calcium carbonate was held on a constant value and the pigments were replaced 1:1. The assessment was done optically **(Table 2)**.

When you compare the results **(Figure 6)**, it is getting obvious that the Sillitin N 82 leads to a yellow shift, which makes the colour more intense while not affecting the opacity of the formulation. That effect was expectable because of the considerable amount of naturally occurring Fe_2O_3 in the Sillitin N 82, which makes colour matching more challenging but enables the reduction of the regular pigment and leads to a feasible cost reduction.

Beside the cost reduction aspect, the easy dispersability of the Sillitin and Silfit in the thermoplastic formulations must also be mentioned because no viscosity reduction by further heating or additional plasticiser is required to realise a homogenous mixture. This effect is beneficial because stronger heating may cause strong discolouration as a result of resin degradation in light coloured formulations and also limit the lifetime of the subsequent road marking.

In the white formulation Silfit Z 91 was used as a regular TiO_2 extender, which leads to a more accurate and homogenous pigment dispersion because the filler particles act as a spacer in between the TiO_2 particles. In this specific formulation a slight blue shift is observable, which might be an indication that low quality TiO_2, originating from a sulphur production process was used in the formulation. This can lead to a yellowing because of side reactions under elevated temperatures, while Silfit Z 91 is totally inert.

For both types of road marking, yellow and white, an increase of the abrasion resistance by the use of Sillitin N 82 or Silfit Z 91 can be expected, which is attributed to the hardness of the Neuburg Silica.

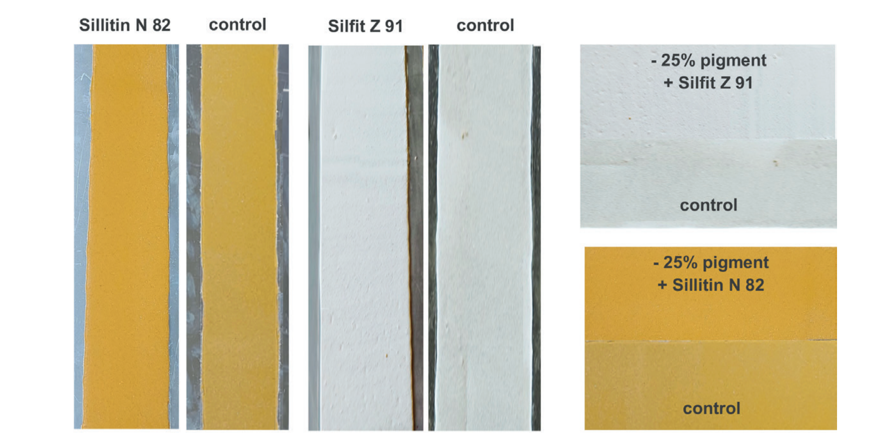

Figure 6. Yellow and white hot melt thermoplastic road marking paint with partial pigment replacement of 25% with Silfit Z 91 (white) and Sillitin N 82 (yellow)

	Control	−40% TiO_2	
Fastrack 53	366	366	366
Foamaster 8034	2.4	2.4	2.4
Triton X 405	2.9	2.9	2.9
AS 238	8.2	8.2	8.2
Titanium dioxide (TiO_2)	96	58	58
Natural calcium carbonate (NCC)	456	399	399
Silfit Z 91		80	80
Amino silane			0.8
Ethanol	11.8	11.8	11.8
Foamaster 8034	0.3	0.3	0.3
Texanol	38	38	38
Water	18.1	18.1	18.1
Total (parts by weight)	**1000**	**985**	**986**

Table 1. Water-based road marking paint formulation (control) and the use of Silfit Z 91 for a partial TiO_2 replacement

	Control	−25% TiO_2
C5 Resin	300	300
Plasticiser	17	17
PE Wax	17	17
Natural calcium carbonate (NCC)	500	500
TiO_2	166	133
Silfit Z 91		33
Total (parts by weight)	**1000**	**1000**

Table 2. White hot-melt thermoplastic road marking formulation (control) and a partial TiO_2 replacement with Silfit Z 91

CONCLUSION

Summarising the presented data, it can be stated that NSE can be utilised to optimise the cost-performance ratio of water- and thermoplastic-based road marking paints for yellow and white formulations. Due to the excellent dispersion properties, the increased hardness, low water uptake and the opportunity to realise a partial pigment replacement, the performance of state-of-the-art coatings can be fine tuned, while the formulation costs are kept at a constant value or even reduced.

Especially, the use of Sillitin N 82 in yellow formulations broadens the field of applications of NSE and emphasises once more the versatility of the Hoffmann Mineral products.

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