# Contents

# Nordkalk Enrich ultrafine PCC enables high performance at high PVC

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Calcium carbonate is a widely used material in many industries e.g. paints and plastics. Usually it is used as a filler to get savings in raw material costs. Generally, it cannot be added in large amounts due to weakening effect of crucial properties such as optical and mechanical properties. How filler behaves is strongly related to its surface properties, such as dispersibility and viscosity of the suspension. Several types of nano-PCC (precipitated calcium carbonate) products are in the market, however, their uses are often restricted to special applications. New product Nordkalk Enrich® is created to break this allegation. Enrich enables high filler loadings without compromising quality. Enrich is also sustainable substitute for traditionally used pigments and crude oil based binders. Furthermore, the multifunctional filler gives rise to new possibilities and performances. The study below demonstrates the potential of multifunctional filler in several applications.

### Nordkalk Enrich at a glance

- Partly replaces $TiO_2$ and binder without weakening crucial properties.
- Gives cost effectiveness for reformulating paint recipes.
- Exists in two forms: stable water dispersion and easy flowing granulated powder.
- Provides multiple formulating options also for other applications such as adhesives

## The unique properties of Nordkalk Enrich

Nano-PCC with primary particle size of e.g. 50 nm has been known and produced in decades. However, the usage of the product has been limited due to the strong agglomeration of the particles. Hence, the true nano scale properties potential have never been really explored until now. A novel nano-PCC product, developed by Nordkalk Corporation is illustrating superior properties and performance. Figure 1 illustrates the particle size distributions of conventional GCC, conventional nano-PCC and Nordkalk Enrich. The conventional GCC has wide particle size distribution and median particle size is 2.5 µm. Minority of particles of conventional nano-PCC are between 0 – 500 nm but the majority of particles are between 1 – 10 µm. Median value for conventional nano-PCC is 3.8 µm and d90% value is 7.2 µm. The particle size of Nordkalk Enrich is between 0 – 500 nm. For Enrich the median is 110 nm and d90% is 240 nm. The figure shows that

Enrich has much narrower particle size distribution than conventional nano-PCC. The optimal size of Enrich particles, close to the half of wave length of the visible light, gives very good hiding power.

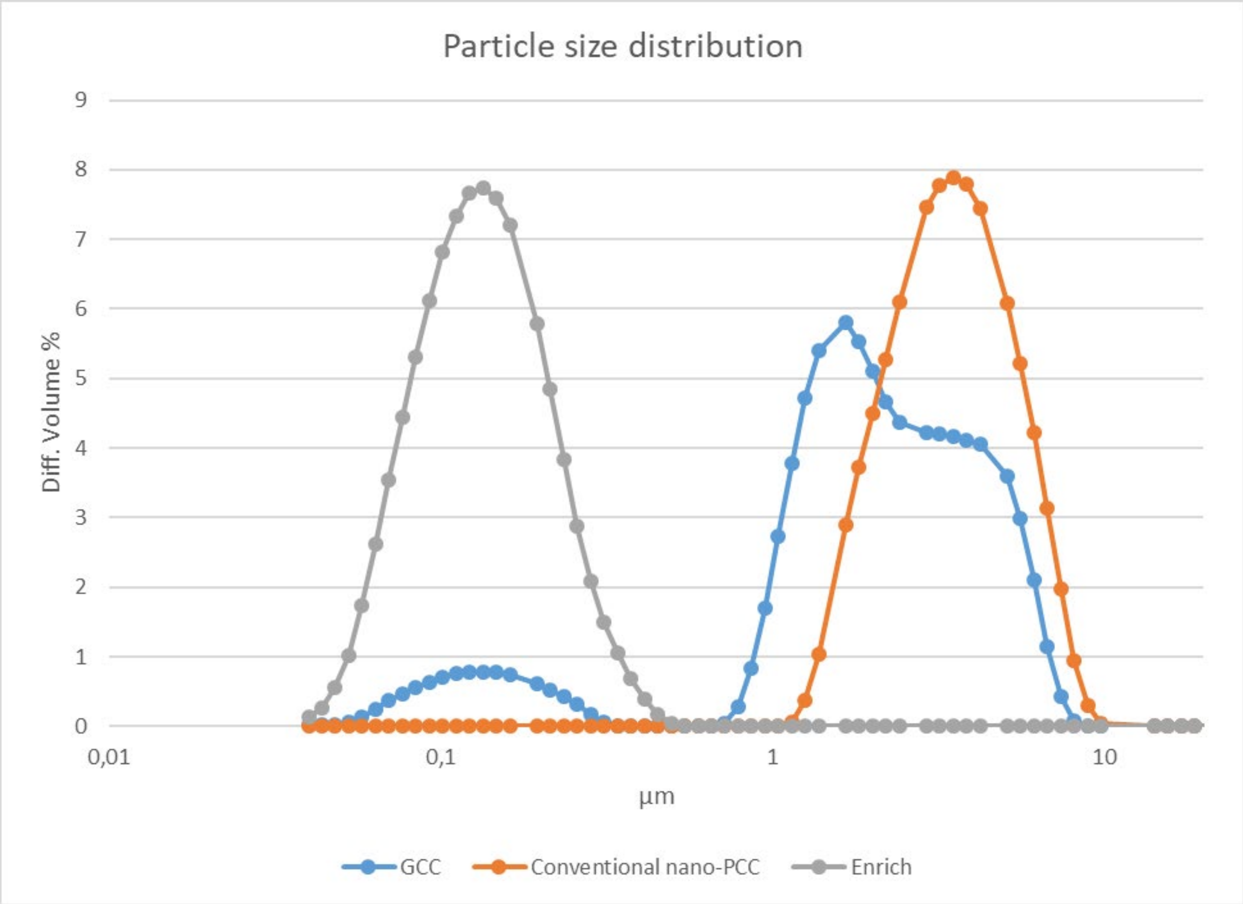
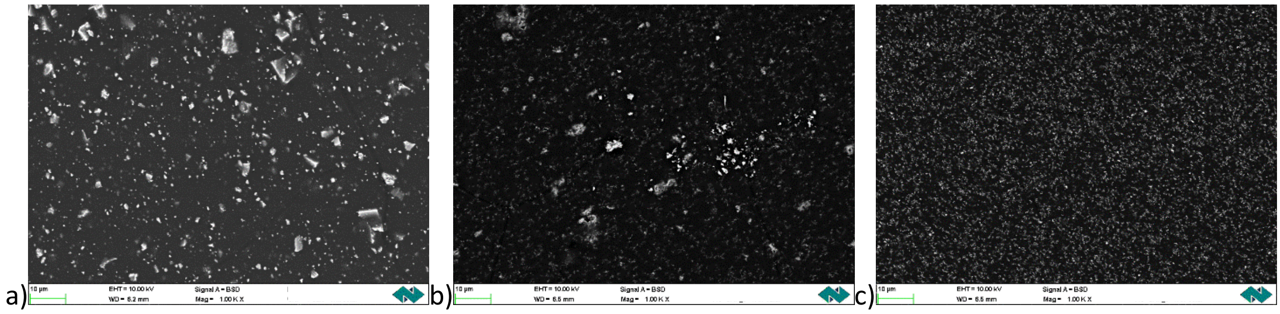


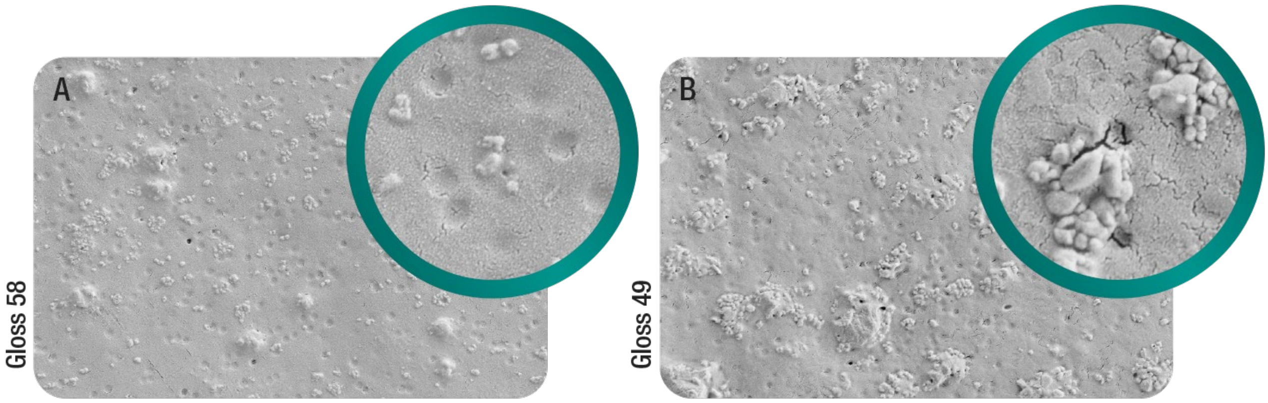

*Figure 1: Particle size distributions of conventional GCC, conventional nano-PCC and Enrich measured with Beckman Coulter LS 13 320 laser diffraction particle size analyzer.*

Scanning electron microscope (SEM) pictures of conventional GCC (Picture 1a), conventional nano-PCC (Picture 1b) and Nordkalk Enrich in a styrene acrylate matrix (Picture 1c) verify the results that the previous particle size distribution results illustrate. SEM pictures were made 1:9 mixes from GCC binder, conventional nano-PCC and binder and Enrich and binder which were mixed 10 minutes with tooth disk agitator. After mixing 200 µm films were prepared and pictures were taken from the films with Zeiss Supra 55VP scanning electron microscope. In the SEM picture you can see that the conventional nano-PCC particles are in large agglomerates. In Picture 1c can be seen well dispersed Enrich particles in primary form or in very small agglomerates. This very good dispersibility enables higher loadings without affecting crucial parameters. Enrich is surface modified with a surfactant which sterically and electro statically prevents re-agglomeration.




*Picture 1: SEM picture (back scatter diffraction method) of a) conventional GCC, b) conventional nano-PCC and c) Nordkalk Enrich in polymer matrix.*

These narrower well dispersed Enrich particles can be seen in Picture 2, comparing a) conventional nano-PCC and b) Enrich. In comparison there can be seen also better surface quality and less cracks caused by GCC, which is also present in these PVC formulations.




*Picture 2: A) PVC filled with Enrich B) PVC filled with conventional nano-PCC*

In order to emphasize the nanorange particle size and the easy dispersibility, Nordkalk Enrich and conventional GCC (ground calcium carbonate) micro filler (d50 % 2.5 µm) were compared in a high gloss indoor paint. The commercial indoor paint was filled with Enrich and GCC filler. Series were made by adding these fillers in to ready paint. They were added by different percentage of dry mass the paint. Dry solid contents in the ready paint and the added filler slurry were the same so consequently, the resulting mix had the same dry solid content. After mixing, 200 µm thick films were prepared, dried for 48 hours and after drying the specular glosses were measured according to standard ISO 2813 with the Zehntner ZLR 1050 M gloss measuring device.

Figure 2 demonstrates gloss as a function of different percentages of filler. Without added filler the gloss (measuring angle 60°) was about 85 %. When GCC is added by 5 % of mass the gloss drops dramatically to value under 50 %. With Enrich the gloss stays almost the same as without filler. When you add 25 % of GCC by mass the gloss has dropped under 10 %. With Enrich the gloss stays over 70 % even if it is added by 40 % of mass. The results correspond to the theory that small particles forms smoother film and the particles pack tighter. This enables higher gloss even with higher PVC's.

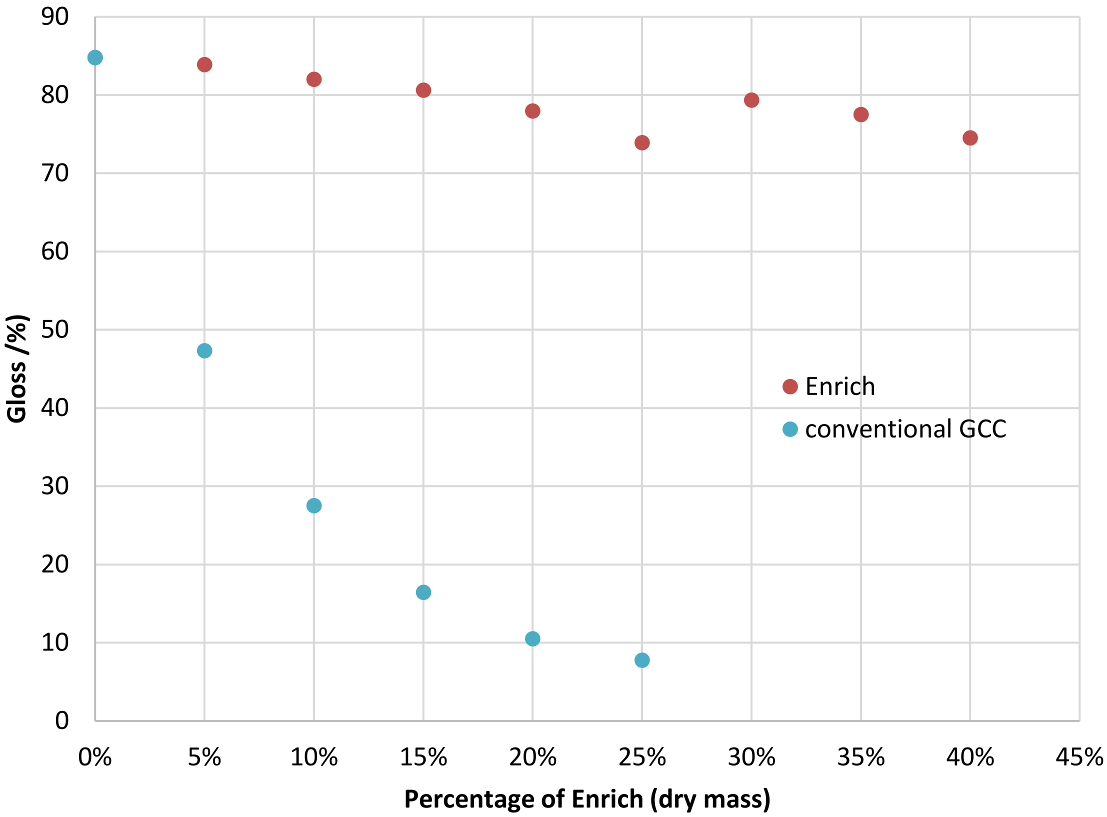



*Figure 2: Gloss values of commercial high gloss indoor paint filled with different percentages of Enrich and conventional GCC.*

## Formulating paints with Nordkalk Enrich

The effect of Enrich's on different coating applications was studied. Conventional nano-PCC and conventional GCC were used as reference materials. The test series in an outdoor paint was made according to Table 1. The reference formulation was altered by replacing binder with Enrich and GCC. The binder was replaced with filler by 20, 25, 30, 35 and 40 % and titanium dioxide by 25 %. Otherwise the paint formulations were kept alike. After mixing the 200 µm thick films were prepared, dried for 48 hours and after drying the specular glosses were measured according to standard ISO 2813 with the Zehntner ZLR 1050 M gloss measuring device.

*Table 1: Formulations used in outdoor paint.*

| | Ref | | | GCC | | | Enrich | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Enrich (dmc 50 %) (%)** | 0,0 | 0,0 | 0,0 | 0,0 | 0,0 | 0,0 | 19,0 | 21,6 | 24,3 | 26,9 | 29,6 |
| **binder (dmc 50 %) (%)** | 52,0 | 41,6 | 39,0 | 36,4 | 33,8 | 31,2 | 41,6 | 39,0 | 36,4 | 33,8 | 31,2 |
| **TiO2 (%)** | 15,6 | 11,7 | 11,7 | 11,7 | 11,7 | 11,7 | 11,7 | 11,7 | 11,7 | 11,7 | 11,7 |
| **Micro fillers (%)** | 0,0 | 8,9 | 10,1 | 11,3 | 12,6 | 13,8 | 0,0 | 0,0 | 0,0 | 0,0 | 0,0 |
| **additives (%)** | 6,6 | 6,6 | 6,6 | 6,6 | 6,6 | 6,6 | 6,6 | 6,6 | 6,6 | 6,6 | 6,6 |
| **water (%)** | 25,8 | 31,2 | 32,6 | 33,9 | 35,3 | 36,7 | 21,1 | 21,1 | 21,0 | 21,0 | 20,9 |
| **total (%)** | 100,0 | 100,0 | 100,0 | 100,0 | 100,0 | 100,0 | 100,0 | 100,0 | 100,0 | 100,0 | 100,0 |
| **PVC (%)** | 13,4 | 25,1 | 27,8 | 30,6 | 33,6 | 36,8 | 25,1 | 27,8 | 30,6 | 33,6 | 36,8 |

Two indoor paint, gloss 20 and gloss 7 were tailored from the original paint formulation. In the tailored formulations the PVC values were increased by adding Enrich. The original and tailored formulations are illustrated in Table 2. Films were prepared and glosses measured according to aforementioned example in outdoor paints.

*Table 2: Formulations used in indoor paints.*

| | Indoor paint gloss 20 | | Indoor paint gloss 7 | |
|---|---|---|---|---|
| | **Original** | **Tailored** | **Original** | **Tailored** |
| **Enrich (dmc 50 %)** | 0,0 % | 17,2 % | 0,0 % | 17,8 % |
| **binder (dmc 50 %)** | 48,8 % | 38,0 % | 32,6 % | 25,5 % |
| **TiO2** | 19,9 % | 17,1 % | 19,9 % | 16,1 % |
| **Micro fillers** | 7,1 % | 6,1 % | 8,5 % | 11,2 % |
| **additives** | 6,3 % | 5,4 % | 12,4 % | 8,9 % |
| **water** | 17,8 % | 16,3 % | 26,5 % | 20,5 % |
| **total** | 100,0 % | 100,0 % | 100,0 % | 100,0 % |
| **PVC** | 24,90 % | 35,43 % | 36,10 % | 49,25 % |

The investigation of the Enrich's effect on floor paint was carried out by formulating with different types of binders. The first formulation comprises of 50 % of polyurethane (PU) and 50 % of soft acrylate (PA(S)). Second formulation was made with 50 % of hard acrylate (PA(H)) and 50 % of soft acrylate (PA(S)). The third formulation was made with 13.4 % of Enrich, consequently 40 % of binder is replaced. Binder in this formulation is soft acrylate (PA(S)). The formulations used are summarized in Table 3. For abrasion resistance tests 200 µm films were made and dried for 24 h in 50 °C. Dried films were weighted before abrasion resistance tests. Abrasion resistance tests where made with Taber 5135 Abraser, abrading wheel was CS-10, load used was 500 g and abrasion time was 1000 cycles. After abrasion the films were weighted again to get loss of mass. Pull-of tests for adhesion were made with DeFelsko PosiTest AT-A adhesion tester according to ISO 4624.

*Table 3: Formulations used in floor paint.*

| | PU/PA(S) | PA(S)/PA(H) | Tailored |
|---|---|---|---|
| **Enrich (dmc 50 %)** | 0,0 % | 0,0 % | 26,8 % |
| **polyurethane (dmc 50 %) PU** | 33,9 % | 0,0 % | 0,0 % |
| **hard acrylate (dmc 50 %) PA(H)** | 0,0 % | 33,9 % | 0,0 % |
| **soft acrylate (dmc 50 %) PA(S)** | 33,9 % | 33,9 % | 41,1 % |
| **TiO2** | 15,2 % | 15,2 % | 15,2 % |
| **additives** | 16,9 % | 16,9 % | 16,9 % |
| **total** | 100,0 % | 100,0 % | 100,0 % |

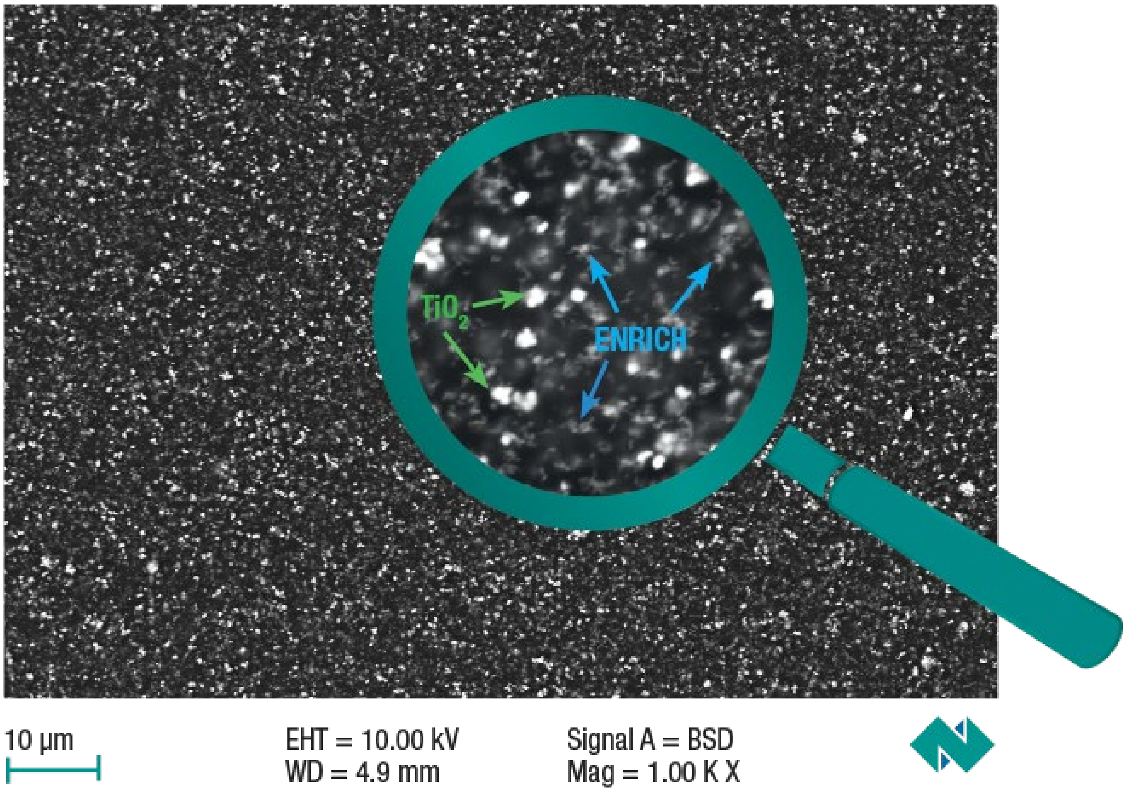
## Multifunctionality offers opportunities in coatings formulations

Enrich was tested in a traditional gloss outdoor paint. In Figure 3 the gloss is represented as a function of PVC. PVC value of reference outdoor paint is 14 % and the gloss at this PVC value is 65 %. When the paint is filled with Enrich the same gloss value is reached with PVC of 30 %. Enrich enables two times higher PVC value without decreasing the gloss value. Summary of all properties is shown in Table 4.

*Table 4: Properties of original and tailored outdoor paint.*

| | | Original | Tailored |
|---|---|---|---|
| **Gloss 60° (%)** | | 65 | 65 |
| **Hiding power** | | good | same as original |
| **Density (g/cm³)** | | 1,17 | 1,19 |
| **Water-vapour transmission (g/m²/24h)** | | 1,3 | 1,6 |
| **Viscosity (cP)** | **1 rpm** | origin | same as original |
| | **20 rpm** | origin | same as original |
| | **100 rpm** | origin | same as original |
| **UV resistance** | | good | good |
| **Adhesion (N/mm²)** | **concrete** | >2 | >2 |

Titanium dioxide was also replaced with Enrich by 15 %. At this $TiO_2$ replacement the hiding power remained the same as in reference paint. SEM Picture 3 shows well how Enrich particles prevents $TiO_2$ from crowding and in that way enables good hiding power with less pigment.




*Picture 3: SEM picture of Enrich and titanium dioxide in binder matrix.*

An explanation for a high gloss with higher PVC value is attributed to the coating surface properties, the smoother the surface the higher the gloss. The film is smoother because the Enrich particles are better dispersed in the paint matrix than conventional particles.

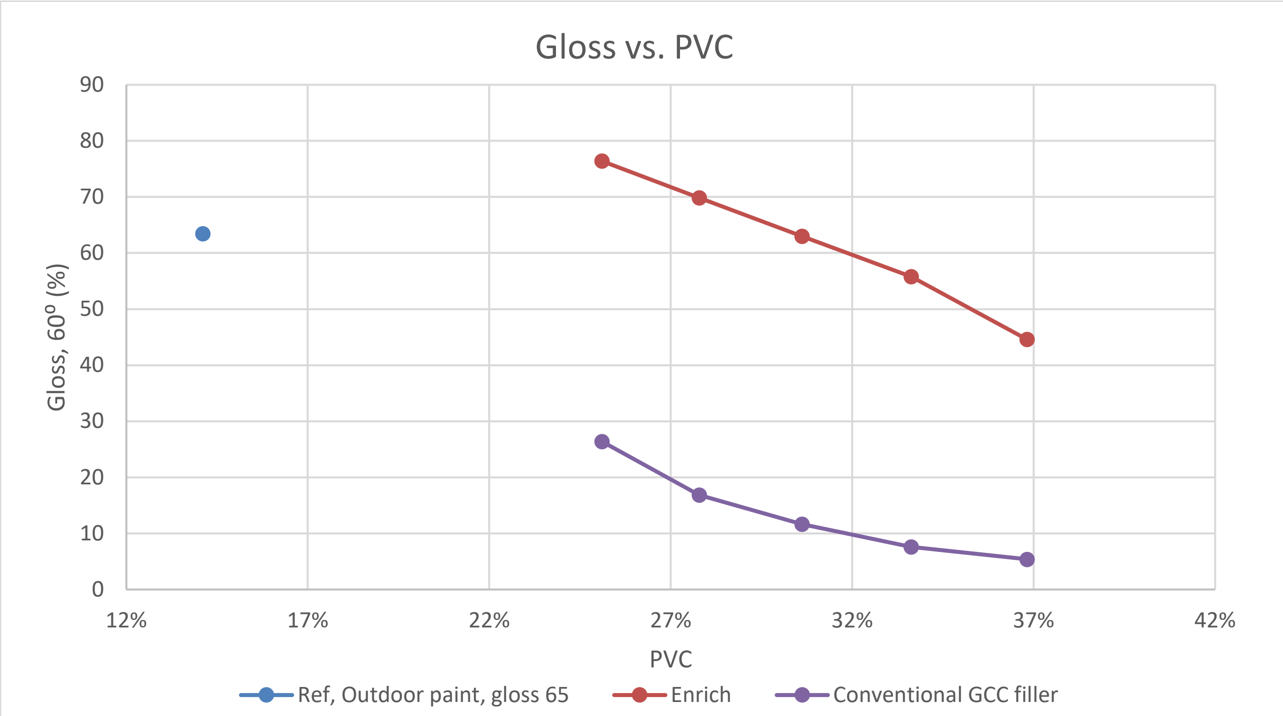



*Figure 3: Gloss values of traditional gloss outdoor paint with different PVC values when binder is replaced with different amounts of Enrich or GCC.*

Two indoor paint formulations were tailored with Enrich. In both formulations PVC values were increased over 10 percent. In Table 5 result including gloss, density and wet-scrub abrasion from original and tailored formulations are summarized. It can be seen that the gloss values are comparable to the reference points. Density values in tailored formulation are a little higher due to the bigger amount of filler, but the difference is not that significant. All wet-scrub abrasion values were below the critical level of 5 µm, thus achieving the wet-scrub classification level of 1. Other critical parameters such as dye tinting and rheology of the paint were also kept at the same level.

*Table 5: Properties of original and tailored indoor paint.*

| | | Indoor paint gloss 20 | | Indoor paint gloss 7 | |
|---|---|---|---|---|---|
| | | **Original** | **Tailored** | **Original** | **Tailored** |
| **Gloss (%)** | **45°** | 19 | 15 | 9 | 9 |
| | **60°** | 23 | 21 | 7 | 8 |
| | **75°** | 52 | 46 | 18 | 21 |
| **Hiding power** | | good | same as original | good | same as original |
| **Density (g/cm$^3$)** | | 1,27 | 1,29 | 1,25 | 1,35 |
| **Wet-scrub abrasion ( µm)** | | 2 | 2 | 2 | 2 |
| **Viscosity (cP)** | **1 rpm** | origin | same as original | origin | same as original |
| | **20 rpm** | origin | same as original | origin | same as original |
| | **100 rpm** | origin | same as original | origin | same as original |
| **Dye tinting** | | origin | good | origin | good |
| **Adhesion (N/mm$^2$)** | **concrete** | >2 | >2 | >2 | >2 |

Explanation to the same gloss values with higher PVC is the same as in the outdoor paint. Wet-scrub abrasion values can also been explained by better packing and minimizing water penetration through the film. Hypothetically, the Enrich particles may form a network with each other and binder particles, giving rise to unique surface interactions and properties. To achieve desired film properties binder needs to be continuum. Enrich shifts this filler binder proportion to higher PVC values.

The abrasion resistance of paint demonstrates the capability of paint to endure abrasive forces. Enrich improves the abrasion resistance. When paint is filled with Enrich, hard binder can be replaced with softer binder. In Figure 4 the abrasion resistance of a commercial floor paint containing polyurethane and soft acrylate (PU/PA(S)), commercial floor paint containing hard acrylate (PA(H)) and floor paint comprising of Enrich and soft acrylate is illustrated. The results demonstrates that paint filled with Enrich has as equally good abrasion resistance (loss of mass 0,12 g) as a commercial paint with harder polyurethane and acrylate (loss of mass 0,13 g). Commercial floor paint with hard acrylate and soft acrylate shows weaker abrasion resistance (loss of mass 0,21 g).

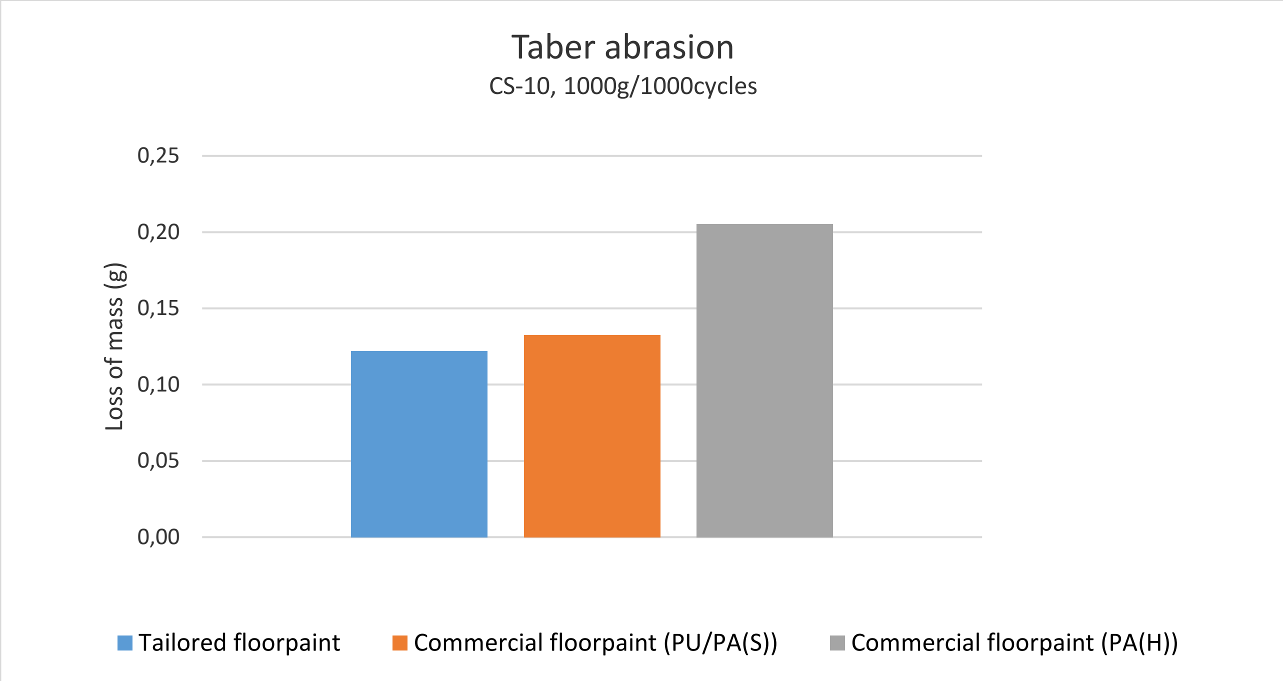



*Figure 4: Abrasion resistances of two commercial floor paints and one floor paint where binder is changed in softer binder and 40 % replaced with Enrich.*

## Enrich in other applications

Nordkalk Enrich provides new formulating opportunities also in several other applications. As a multifunctional filler Enrich can improve several properties and at the same time be cost efficient. Next will be shortly introduced highlights from adhesives, sealants, plastics and rubbers. Enrich has also shown potential in fire retardation and paper applications.

### Adhesives and Sealants

Fraunhofer Institute in Germany has investigated the suitability of Enrich in adhesives and sealants. Even with the small quantities of Enrich the required properties (viscosity, no sedimentation during storage, application ... ) are achieved in combination with higher tensile strength at 100% elongation (2 fold), higher elongation at $F_{max}$ (4 fold), higher elongation at break (3 fold), lower modulus of elasticity at room temperature and very good hydrolysis resistance. Higher tensile strength can be seen in Figure 5. Out of these properties named before, Enrich has also shown reduced drying time in water proofing applications.

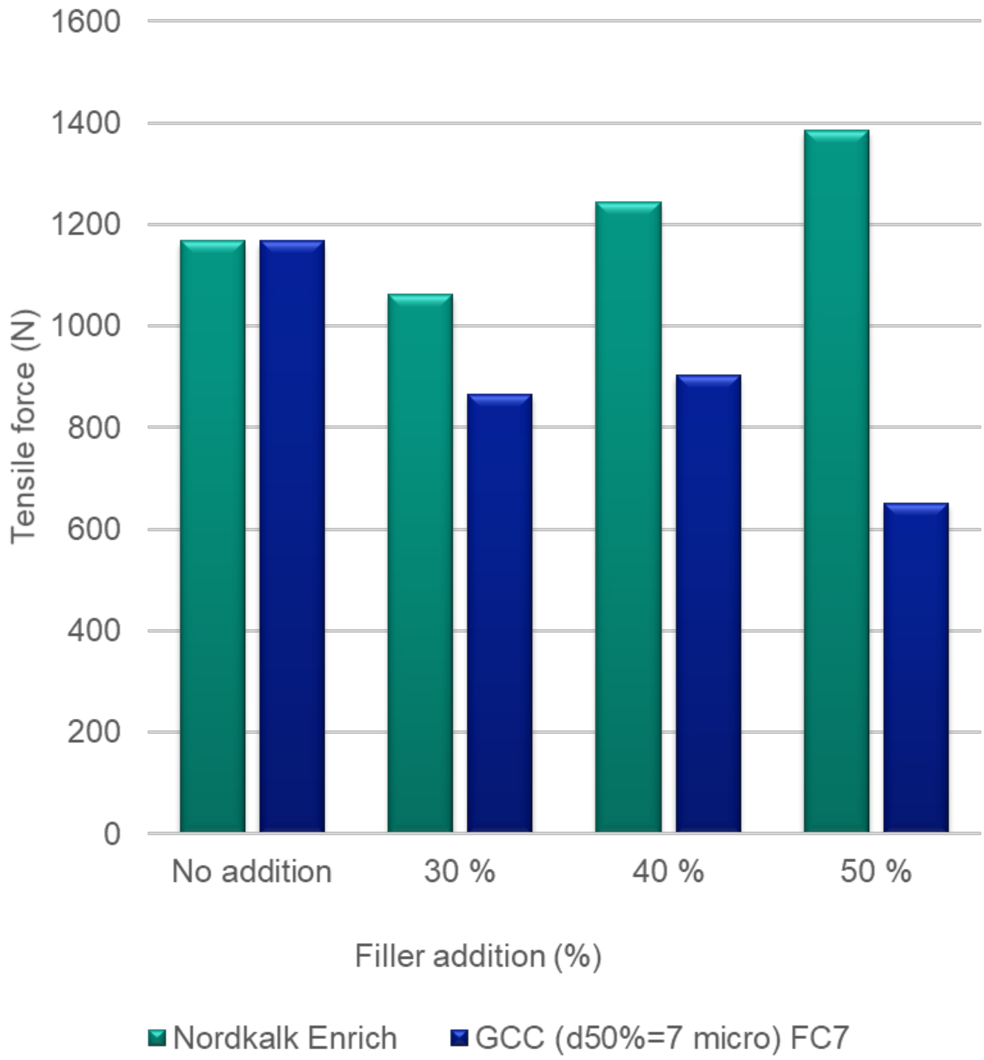
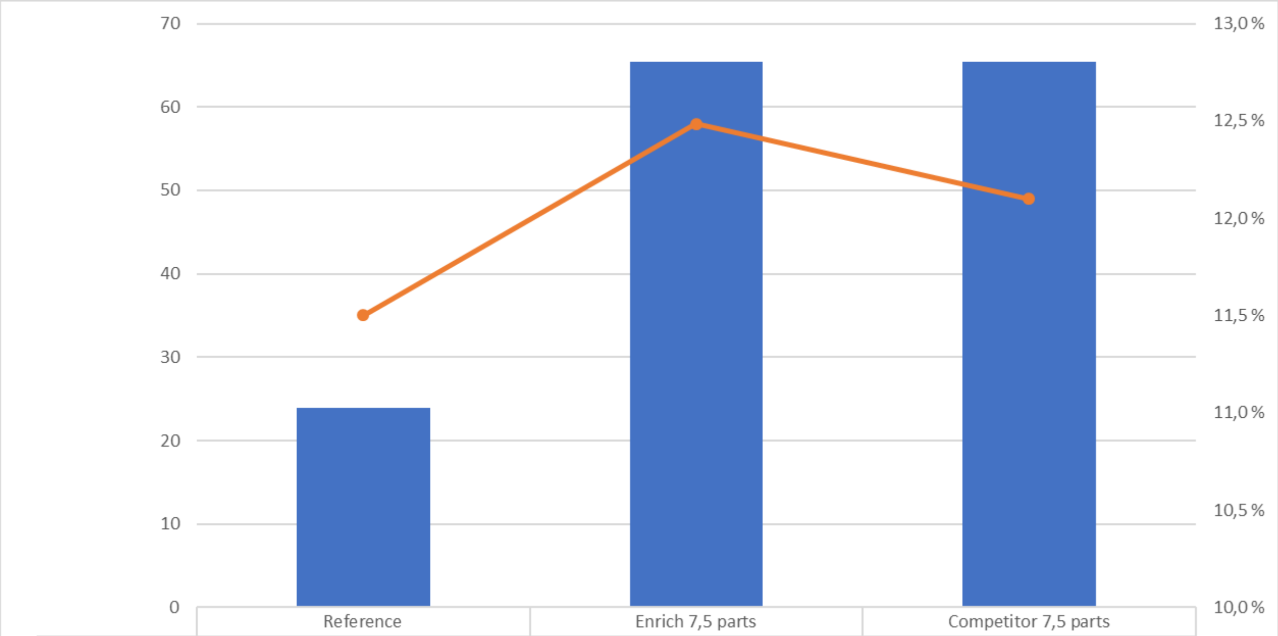



*Figure 5: Tensile strengths of Enrich and ground calcium carbonate in polyvinyl acetate based adhesive*

## Plastic and Rubber

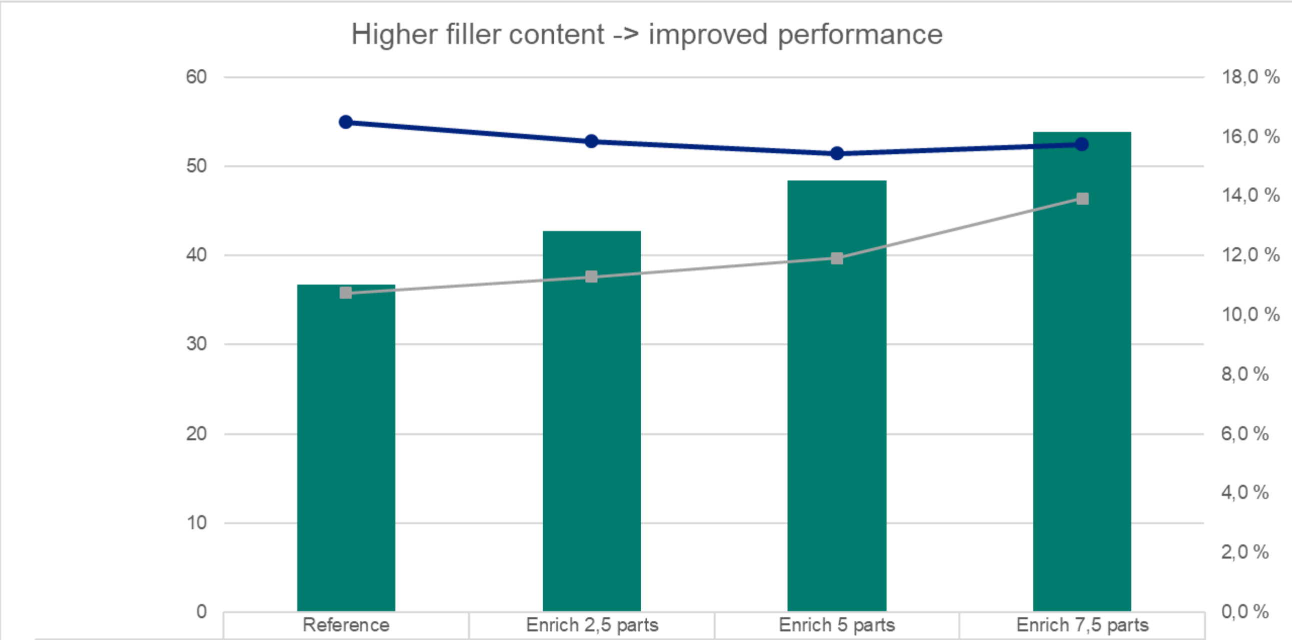
In plastic and rubber Nordkalk Enrich enables higher filler loadings. As it has been already presented in the beginning of the article (Picture 2 a and b) one can see how conventional stearate coated nano-PCC is badly dispersed compered to Enrich. Better dispersibility leads to higher gloss which can be seen from Figure 6.




| | Reference | Enrich 7,5 parts | Competitor 7,5 parts |
|---|---|---|---|
| Filler content | 11,0 % | 12,8 % | 12,8 % |
| Gloss [%] | 35 | 58 | 49 |

*Figure 6: Gloss comparison of PVC filled with Enrich and competitor (conventional nano-PCC)*

Figure 7 illustrates how gloss of PVC increases when it is filled with Enrich. At the same time the impact strength stays more or less on the same level when total filler loading is increased almost by 50%.




| | Reference | Enrich 2,5 parts | Enrich 5 parts | Enrich 7,5 parts |
|---|---|---|---|---|
| Filler content | 11,0 % | 12,8 % | 14,5 % | 16,2 % |
| Gloss (%) | 35,8 | 37,6 | 39,7 | 46,4 |
| Impact strength | 54,9 | 52,7 | 51,4 | 52,5 |

*Figure 7: PVC filled with different loadings of Enrich*

## Conclusion

Results show that in coatings applications high PVC values can be achieved without comprising with technical performance by adding Enrich. With Enrich binder and $TiO_2$ has been partly replaced in high glossy indoor paint and traditional gloss outdoor paint and still were achieved desired gloss and hiding power. In indoor paints gloss 20 and 7 the tailored formulations with the higher PVC has given as good results as reference formulations with lower PVC. The critical values has remain the same and wet-scrub abrasion results has been maintained in class 1. Tailored formulations have covered all the properties they should. In floor paint the binder has been partly replaced with Enrich and also the hard binders has been changed to softer ones. The shift from harder binders to softer hasn't weakened abrasion resistance. In the case of acrylate binders the shift from hard to soft with Enrich in the formulation has even demonstrated superior abrasion resistance properties.

Enrich has shown its multifunctionality also in other applications including adhesives and plastics. Higher filler loadings are possible when using Enrich, still maintaining required properties. Some properties can be even improved in a cost effective way.