

IMPROVING SOILING RESISTANCE WITH THE AID OF NANOPARTICLES

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2 YKI, Institute for Surface Chemistry

YKI, Institute for Surface Chemistry, is the internationally leading industrial research institute in applied surface and colloid chemistry. It is part of the SP Group, SP Technical Research Institute of Sweden. The work within YKI is organized in three sections, Materials and Coatings Section, Forest Products Section and Life Science and Chemical Industry Section. In the Materials and Coatings Section the focus of research is the development and use of new materials and formulations within applications such as coatings, adhesives, personal care products, packaging applications and composites. Furthermore, coatings and surface modifications layers with properties such as anti-soiling, superhydrophobic, scratch resistance, anti-fouling, camouflage and barrier functionalities are developed.

3 Introduction

The reason why objects get painted is to protect them from environmental influences like humidity, mold growth, sunlight, dust etc. but they get also painted for decorative reasons to give them a nice appearance. To protect and maintain the painted object it is necessary to create a paint which can withstand all these environmental factors because a better resistance results in less frequent repainting, cleaning or maintenance of the object which saves material (e.g. solvents and biocides) and money. The aim of this project is to find a way to get a better soiling resistance with the aid of nanoparticles.

But is it possible to improve the dirt pick-up resistance of exterior paints by adding silica nanoparticles? Earlier tests showed that the application of colloidal silica nanoparticles gives an increased coating hardness [1] and a higher hardness leads to a better soiling resistance [2]. But what role does the binder play on which the four different paints are based (Acrylate, Acrylate reinforced with Alkyd, Alkyd reinforced with Acrylate and Alkyd)? What happens at an increased temperature up to 50°C, e.g. during heavy sunlight exposure when the paints become tacky due to their thermoplasticity.

For all tests commercial paints were used as a tinting base to be able to compare the results to industrial use. This will also give a notion on how the nanoparticles behave in the presence of other particles.

Another question is how the composition of the dirt effect the soiling tendency? The composition of the dirt depends on the location if it is urban or rural [3]. In an urban area a high amount of carbon is detected e.g. diesel soot from heavy traffic and firing plants. However in rural places the dirt contains less carbon and the dominating material is inorganic dust of minerals and biogenic material from plants, pollen, spores [3].

To measure the degree of the dirt pick-up the change of the color or more exactly the “whiteness” and the “redness” were determined with a spectrophotometer. The Lab-values were obtained and the ΔL and Δa were evaluated.

A critical state of a freshly applied paint is the time after the application because then the paint is still tacky and picks up more dirt than usual [2]. The early dirt pick-up resistance is another thing what could be improved with the aid of nanoparticles.

Another question is how to do the contamination tests and how convincing are the results? It already exists an interior testing method but the results are not that clear and therefore the test needed to be improved or a new different procedure has to be developed. To see if there is any correlation between the testing methods the results of the different indoor testing methods will be compared with the results of a long term outdoor exposure, which is still running.

4 Multiparticle systems

Much research has been conducted to find systems and correlations between different particles and their effect on surface properties. Due to the high complexity of current paints and coatings and the high variety of components it is very difficult to try to predict what kind of properties different particles will have.

4.1 Tinting base

A tinting base paint usually consists of a number of components. These components are; one or more binders that holds the paint together. Pigment particles used to give the coating its opacity, usually a titanium oxide. A filling agent, commonly talcum, used to lower the cost of the paint. Some sort of thickener to regulate the viscosity of the paint. There are a wide variety of commercially available tinting bases on the market today used as white outdoor coatings, or mixed with colorants to obtain a suitable color.

5 Nanoparticles

5.1 Colloidal silica

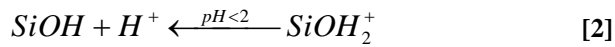
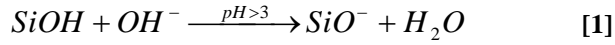
5.2 Properties of colloidal silica

Colloidal silica is a stable dispersion of amorphous silica particles. The silica particles are formed by a network of silicon dioxide or silica. Generally in silica the silicon atom is surrounded by oxygen atoms, with each oxygen atom attached to two Si-atoms.

Dependent on the surface of the silica particle it can be either hydrophilic or hydrophobic [5].

The surface is primarily covered with silanol groups, Si-OH, these groups have the main interaction with water molecules, thus giving a hydrophilic surface. The silanol group has a low point of zero charge, which occurs at pH 2-3, giving the surface a negative charge

at pH levels utilized in most paints (pH 8-9). This is lower than most oxides, which generally have a point of zero charge around pH 5-7 [5]



5.3 Bindzil 40/220

Bindzil 40/220 is colloidal silica with a spherical shape. The average diameter of the particles is 12 nm [6]. The surface is covered with silanol groups giving a negative charge at pH of 2 or more is seen in *Figure 1*. The particles are highly hydrophilic and remain a stable suspension with water for extended periods of time. The stable colloidal solution is transparent and odorless.

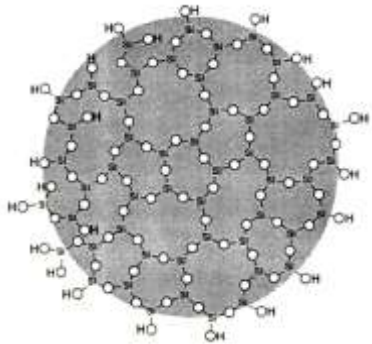


Figure 1: Spherical silica nanoparticle with silanol surface groups.

5.4 Bindzil CC40

The Bindzil CC40 is an epoxysilane modified version of the Bindzil 40/220 [6]. This treatment is done to get an increased hydrophobic surface. Studies show that the silanized silica has an increased compatibility with acrylate monomers, giving an increased

incorporation of the silica particles in the polymer matrix [7]. The Bindzil CC40 particle can be seen in *Figure 2*.

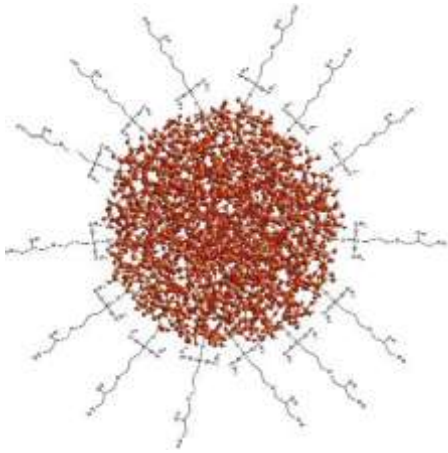


Figure 2: Bindzil® CC 40 Silane modified. [6]

5.5 Applications of colloidal silica

Silica is featured by inert chemical properties and high hardness. Therefore silica is used where high abrasion and scratch resistance is required. Nanosized silica products have been proven to intensify these properties [8, 9]. Other properties that are improved are flame resistance, solvent resistance; block resistance and dirt pick up resistance, due to decreased thermoplasticity [9-11].

6 Materials and Methods

6.1 Chemicals and Materials

Bindzil 40/220 supplied by Eka Chemicals, 40% solid content

Bindzil CC40 supplied by Eka Chemicals, 37% solid content

Butylglycol, supplied by Aldrich, purity 99%

Carbon Black, Carbon Black FW 200 supplied by Degussa AG

Pitch, Special Pitch No 5 supplied by Koppers UK limited

Minerals, JIS test powder 1, class 8 supplied by APPIE

Alkyd paint: "Exponyl Elit Täcklasur", Beckers

Alkyd/ Acrylate paint: "Fönsterfärg", Beckers

Acrylate/ Alkyd paint: "Trähusfärg", Beckers

Acrylate paint: "Bestå Täckfärg Trä", Alcro

Acrylate paint: "Fasadakrylat", Beckers

Primer "Fönstergrund V", Beckers

Primer "Trägrund", Beckers

Sealer "Elit, grundolja", Beckers

Deionised water

Pine tree wood panels, 200x80x20mm, SP Träteck

6.2 Methods

6.2.1 Preparation of the paints

Each type of Bindzil was dispersed with the Dispermat at 3000rpm for 5 minutes into the different paints. The amount of Bindzil was 12.5/ 6/ 3 wt% (as supplied). A higher amount than 12.5wt% of Bindzil was not possible to apply properly because of the high viscosity.

Table.1: Composition of the paints (12.5wt% of Bindzil dispersion) Recipe for 60g

	mass [g]
Paint	45
Bindzil	7.5
H ₂ O	7.5
Total	60

Table.2: Composition of the paints (6wt% of Bindzil dispersion) Recipe for 60g

	mass [g]
Paint	48.9
Bindzil	3.6
H ₂ O	7.5
Total	60

Table.3: Composition of the paints (3wt% of Bindzil dispersion) Recipe for 60g

	mass [g]
Paint	50.7
Bindzil	1.8
H ₂ O	7.5
Total	60

6.2.2 Preparation of the dirt solution

The dry components were mixed in a mortar and then the pitch was added and stirred in manually. 1g of the dirt was mixed with 1g Butylglycol and these 2g were filled in a spray bottle and filled up with 998g deionised water.

Table.4: Recipe of 50g of “standard dirt”

	mass [g]
Carbon black (Degussa)	8.5
Minerals (APIIE, Japan)	35
Pitch (Koppers)	6.5
Total	50

Table.5: Recipe of 10g of “hydrophobic dirt”

	mass [g]
Carbon black (Degussa)	10
Total	10

Table.6: Recipe of 10g of “hydrophilic dirt”

	mass [g]
Minerals (APIIE, Japan)	10
Total	10

Table.7: Recipe of the dirt solution of “standard dirt”

	mass [g]
Standard dirt mixture	1
Butylglycol	1
H ₂ O	998
Total	1000

Table.8: Recipe of the dirt solution of “hydrophobic dirt”

	mass [g]
Carbon black (Degussa)	1
Butylglycol	1
H ₂ O	998
Total	1000

Table.9: Recipe of the dirt solution of “hydrophilic dirt”

	mass [g]
Minerals (APIIE, Japan)	1
Butylglycol	1
H ₂ O	998
Total	1000

6.2.3 Procedure of contamination

The samples were set up in a 45° angle and the samples got sprayed with the dirt solution for 3 times with one minute between each spraying. The distance between the spray bottle and the samples was 30-40cm. The maximal possible pressure of the bottle was used to perform each spraying. After the contamination the samples were left for 1 day for drying. After drying the samples were rinsed with deionised water. The L- value (a- value when the hydrophilic dirt was used) was measured before and after the contamination. After rinsing the L- value (a- value) was measured again.

6.2.4 Procedure of heated contamination

The contamination was conducted in the same way like above but immediately after each spraying the samples were left in an oven at 50°C for 1 hour. 3 cycles of heating + spraying were conducted. The L- value (a- value) was measured before contamination, after each spraying/ heating cycle and after rinsing.

6.2.5 Rheology measurements

For the rheological measurements the “Gemini” from “Bohlin Instruments” with a cylindrical system and the following parameters was used:

shear rate: 0.1 – 200 ; 200 – 0.1 [1/s]; time: 281.8 s; temperature: 25°C; 5s delay time

6.2.6 Effect of cure time on soiling

We tested how the soiling tendency was affected by the time of curing. The samples were prepared and contaminated after 1 day, 7 days and 18 days of curing. The samples were sprayed 3 times and left for drying over night. The L- values (a- values) were measured before and after contamination. After rinsing the L- values (a- values) were measured

again. The dirt solutions, which were used for contamination, were the hydrophilic and the hydrophobic dirt solution.

6.2.7 Outdoor long term exposure

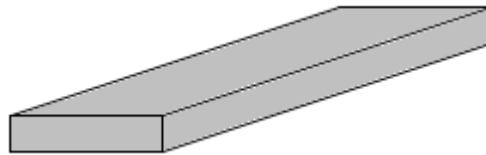
The preparation of the samples is oriented at Swedish standard method [4].

The samples which were used for the exposure were pine tree panels with the sizes 200x80x20 mm. 10 replicates per paint were prepared, 9 for outdoor exposure and one was kept as a reference indoor. At first all the panels were treated with a primer, “Fönstergrund V” for the “Fönsterfärg” mixture and “Trägrund” was used for all the other paints.

All sides of the panels were primed except the backside (1).

After a few days the paints were applied on the top and both sides (2). The primer and the paints were applied by brush. The last step was the sealing with the “Grundolja”. The ends were sealed by dipping (3).

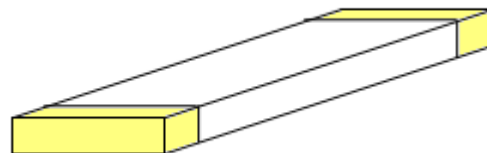
1) Primer



2) Paint application



3) Sealing



The samples were set up in a 45° angle facing south and they were placed randomly on the rack at the test field in Bogesund.



Figure 3: Sample rack at the test field of “Trätek” in Bogesund

7 Results

7.1 Results “Exponyl”

7.1.1 Pendulum Hardness

The measurement was conducted after 4 days of curing. The pendulum hardness increased with 43% for CC40 and 29% for the 40/220 silica nanoparticles. The amount of added silica was 25 wt%.

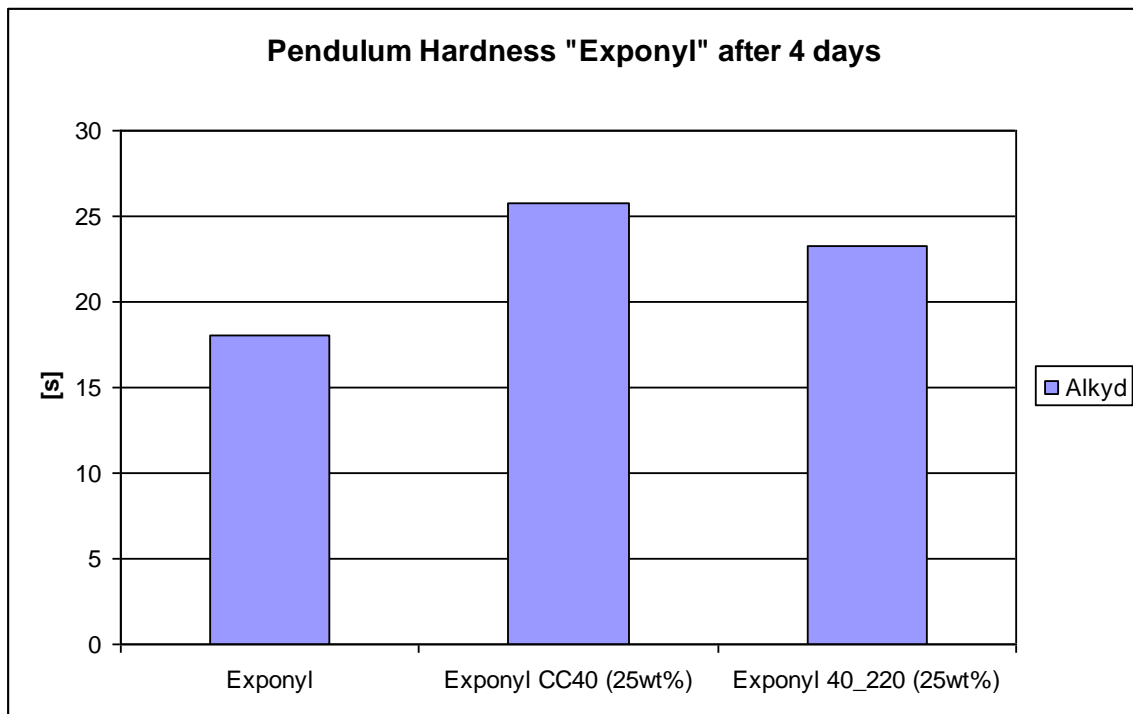


Figure 4: Pendulum Hardness results of the alkyd paint (“Exponyl”) with and without nanoparticles

7.1.2 Rheology

The addition of the silica nanoparticles has no dramatic effect on the rheological behavior of the Exponyl dispersions.

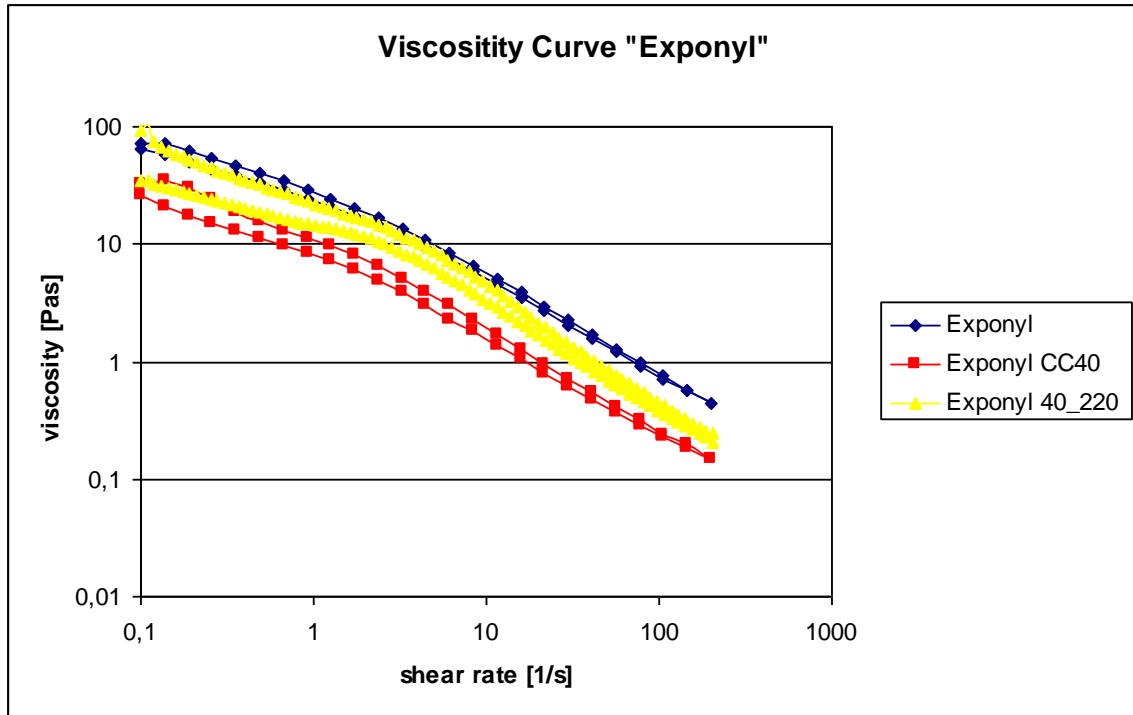


Figure 5: Viscosity curve of the alkyd paint "Exponyl"

7.1.3 Results: “Early dirt pick- up” with standard dirt

The dispersions with the silica show a better soiling resistance compared with the tinting base after 2h and 24h of curing but in general the dirt pick-up increases with a longer cure time. After 2h the CC40 shows 56% less dirt pick-up than the tinting base and after 24h it is still 18% less. The 40/220 shows after 2h of curing 93% less dirt pick-up and after 24h it is almost the same. After 30 days of curing the dirt pick-up of the dispersion with the silica is 30% and 22% higher than the pick-up of the tinting base.

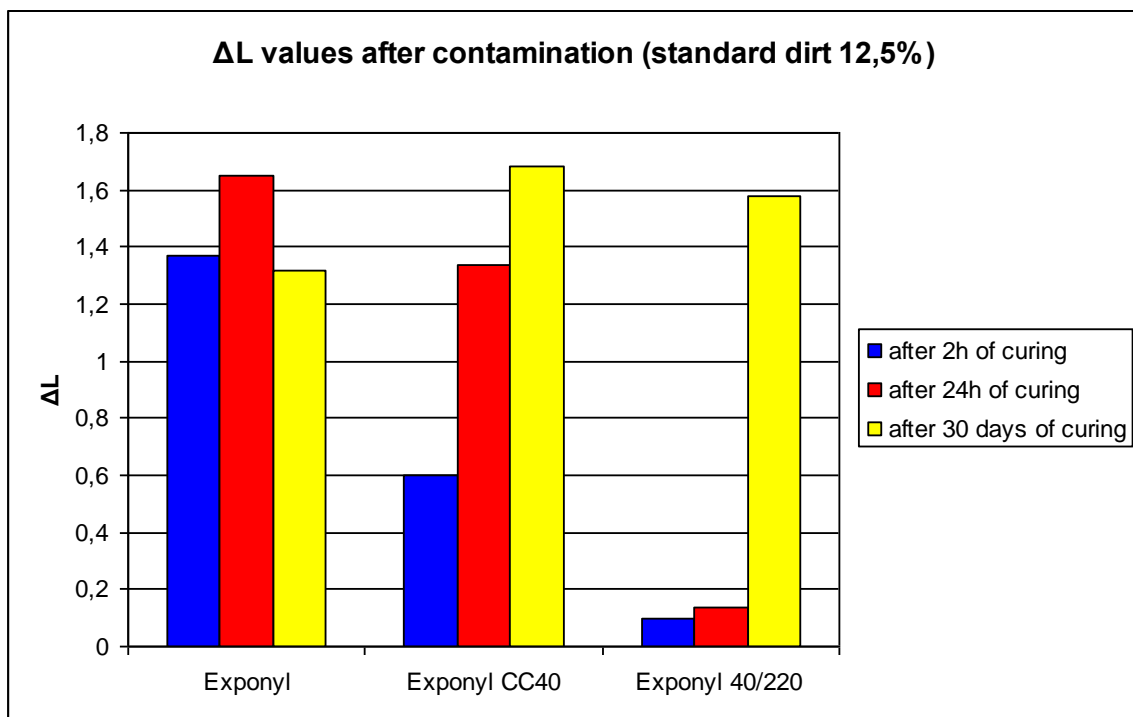


Figure 6: ΔL values of “Early dirt- pick-up” test

7.2 Results “Fönsterfärg”

7.2.1 Pendulum Hardness

The measurement was conducted after 4 days of curing. The pendulum hardness increased with 75% for CC40 and 39% for the 40/220 silica nanoparticles. The amount of added CC40 was 25 wt% and just 12,5wt% of the 40/220 because it has a strong effect on the viscosity.

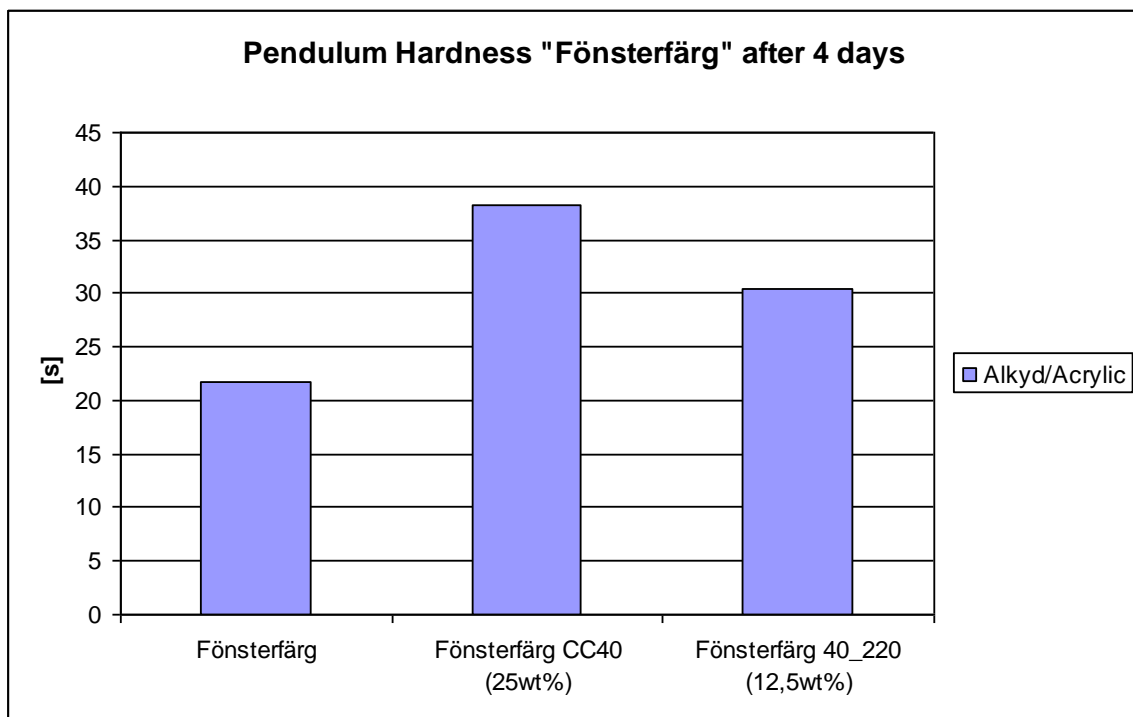


Figure 7: Pendulum Hardness results of the alkyd/ acrylate paint (“Fönsterfärg”) with and without nanoparticles

7.2.2 Rheology

The addition of the silica nanoparticles has no drastic effect on the rheological behavior of the “Fönsterfärg” dispersions.

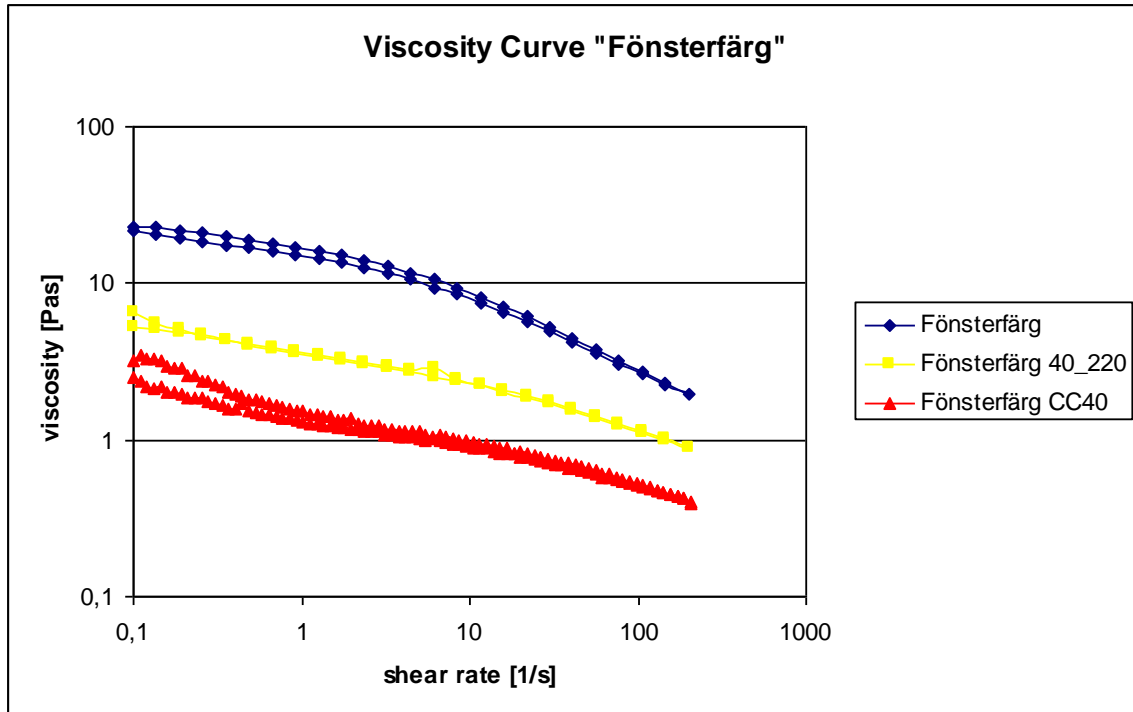


Figure 8: Viscosity curve of the alkyd/ acrylate paint "Fönsterfärg"

7.3 Results: “Trähusfärg”

7.3.1 Pendulum Hardness

The measurement was conducted after 4 days of curing. The pendulum hardness increased with 117% for CC40 and 79% for the 40/220 silica nanoparticles. The amount of added CC40 was 25 wt% and just 12,5wt% of the 40/220.

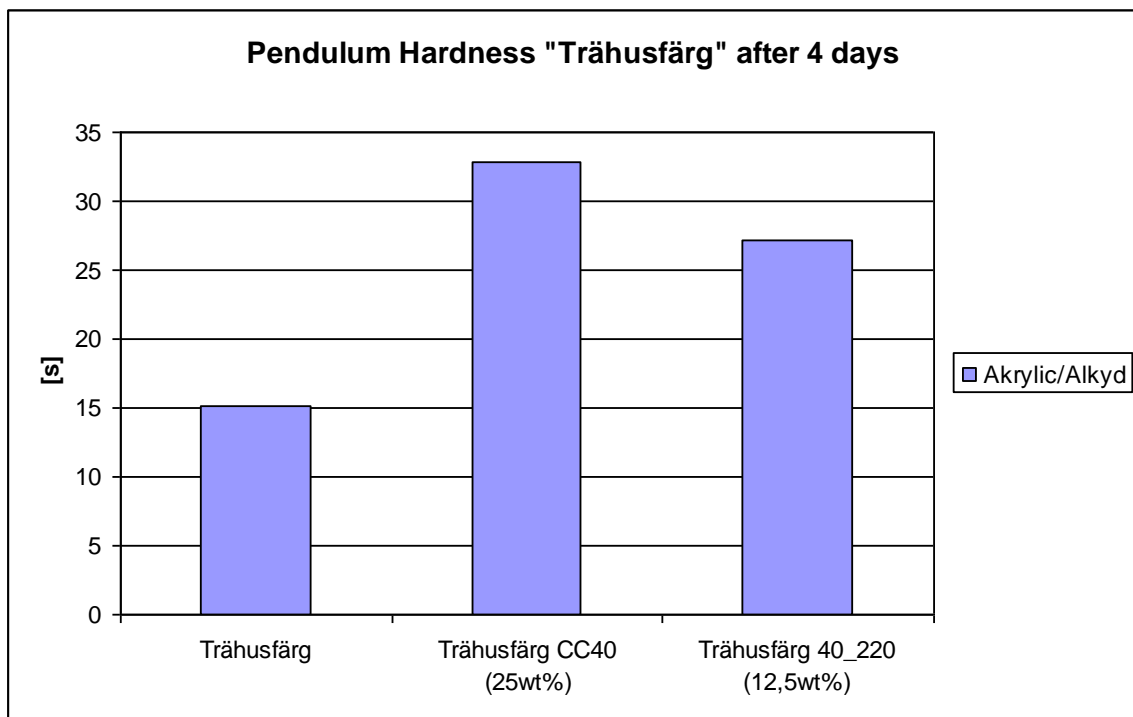


Figure 9: Pendulum Hardness results of the acrylate/ alkyd paint “Trähusfärg” with and without nanoparticles

7.3.2 Rheology

The addition of the silica nanoparticles has no drastic effect on the rheological behavior of the “Trähusfärg” dispersions.

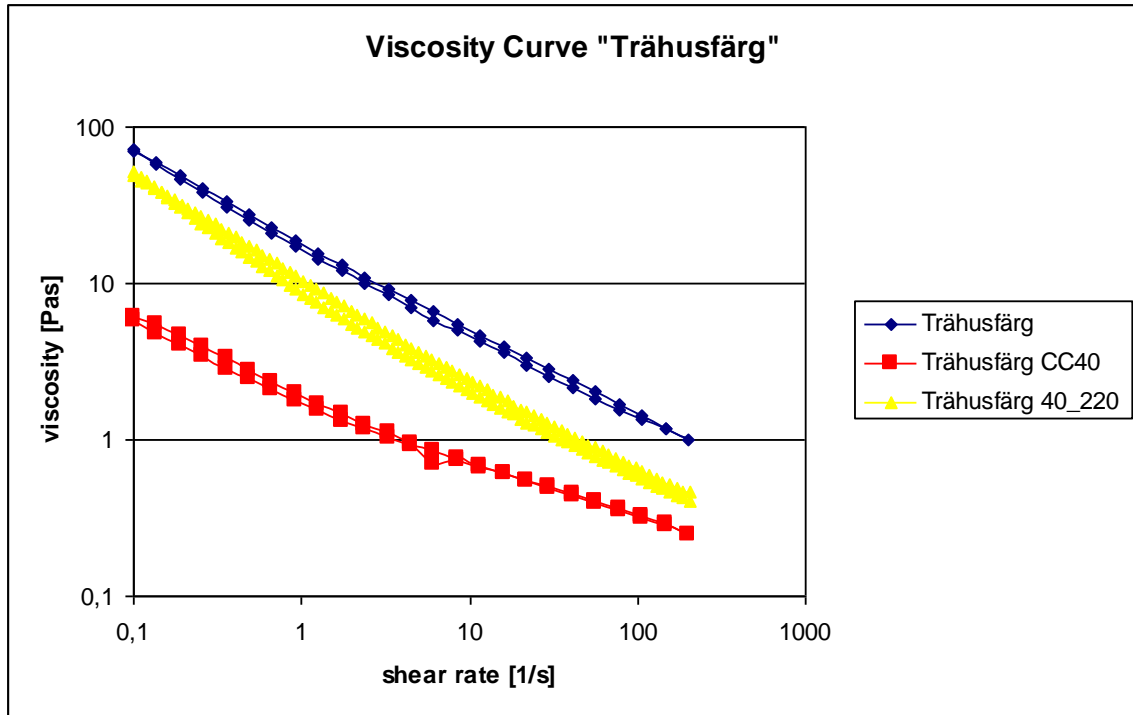


Figure 10: Viscosity curve of the acrylate/alkyd paint “Trähusfärg”

7.4 Results: “Bestå”

7.4.1 Pendulum Hardness

The measurement was conducted after 4 days of curing. The pendulum hardness increased with 40% for CC40 and 45% for the 40/220 silica nanoparticles. The amount of added silica was 12.5wt%.

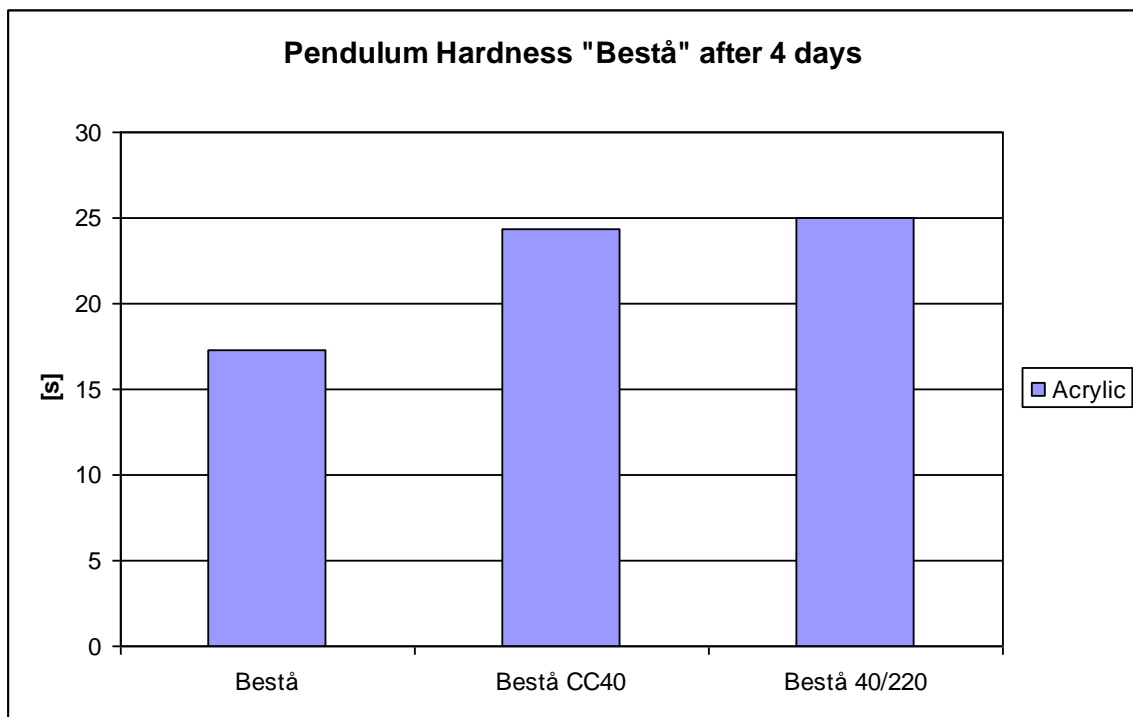


Figure 11: Pendulum Hardness results of the acrylate paint “Bestå” with and without nanoparticles

7.4.2 Rheology

For the rheology measurements another acrylate paint was used, “Fasadakrylat” (Beckers) which is very similar to the “Bestå”. The addition of the silica nanoparticles has no dramatic effect on the rheological behavior of the Fasadakrylat dispersions.

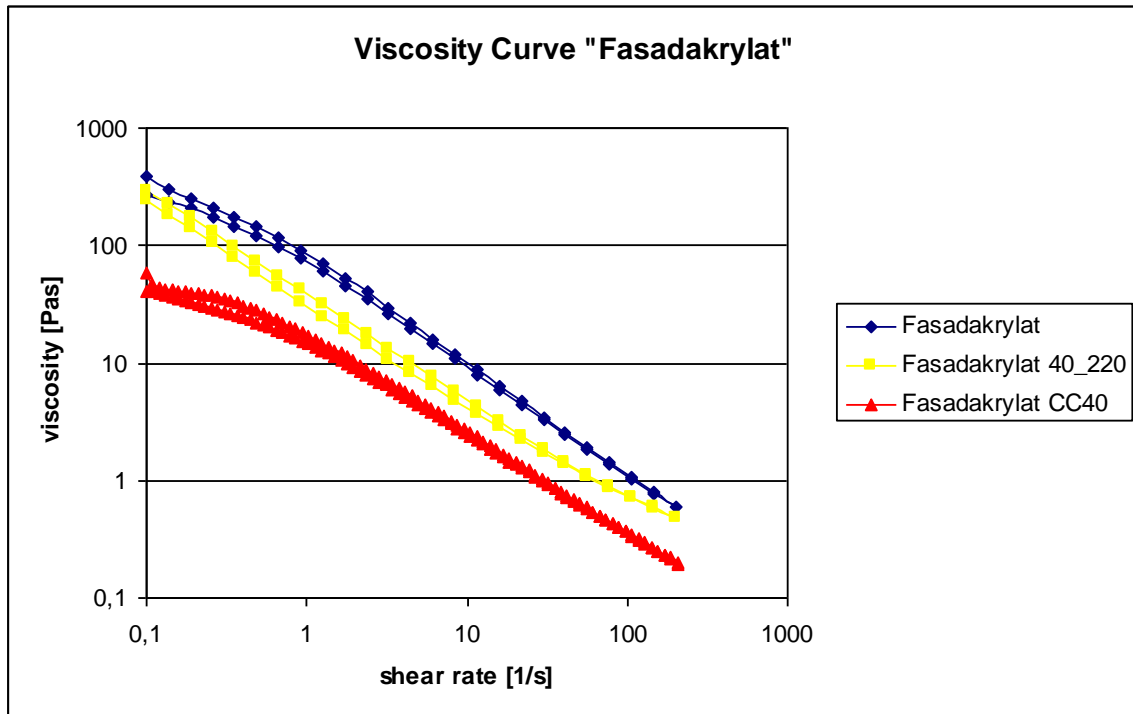


Figure 12: Viscosity curve of the alkyd paint “Fasadakrylat”

8 Results of the laboratory dirt- contamination tests

8.1 Results: Dependency of cure time with Hydrophobic/ Hydrophilic dirt

8.1.1 Results: Dependency of cure time with hydrophobic dirt

The contamination tests with hydrophobic dirt show that all dispersion with silica nanoparticles have a higher soiling resistance and it is getting better with a longer cure time except the alkyd 40/220 which is 8% less resistant than the tinting base after 18 days of curing. In general the alkyd dispersions improve least of all. The strongest effect shows the acrylate paint “Bestå”. The resistance with CC40 is improved for 48% after 1 day of curing. The 40/220 improves the resistance after 1 day of curing for 54%. The other dispersions are somewhere in between.

The ΔL value after rinsing is not displayed because it has almost no effect and the dirt stays on the sample.

Ranking of the dispersions:

1. acrylate/alkyd 40/220
2. acrylate 40/220
3. alkyd/acrylate 40/220
4. acrylate/alkyd CC40
5. acrylate CC40
6. acrylate/alkyd
7. alkyd/acrylate CC40
8. alkyd/acrylate
9. alkyd 40/220
10. alkyd CC40
11. acrylate
12. alkyd

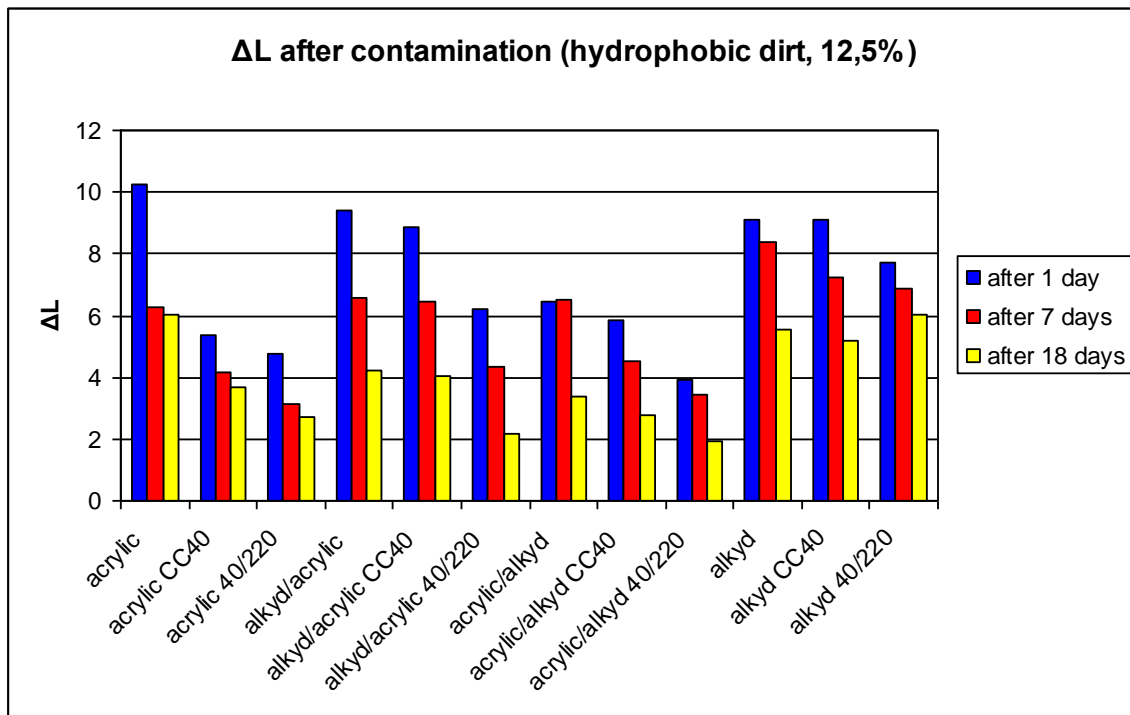


Figure 13: ΔL values of cure time dependent contamination with "hydrophobic dirt"

8.1.2 Results: Dependency of cure time with hydrophilic dirt

The tests with the hydrophilic dirt show that the addition of silica improves the soiling resistance of all dispersions. A longer cure time improves the resistance as well, except after 18 days the dirt pick-up is enormously high compared to the pick-up after 1 day and 7 days but you can still see the tendency that the dispersions with silica have a better resistance except the alkyd/acrylate paints with silica they have a higher dirt pick-up than the tinting base. The alkyd dispersions show the strongest effect with the silica of all dispersions.

The Δa value after rinsing is not displayed because it has almost no effect and the dirt stays on the sample.

Ranking of the dispersions:

1. acrylate/alkyd 40/220
2. alkyd/acrylate 40/220
3. acrylate/alkyd CC40
4. alkyd/acrylate CC40 (same result like acrylate/alkyd CC40)
5. alkyd/acrylate
6. alkyd CC40
7. acrylate 40/220
8. alkyd 40/220 (same result like acrylate 40/220)
9. acrylate CC40
10. acrylate/alkyd
11. acrylate
12. alkyd

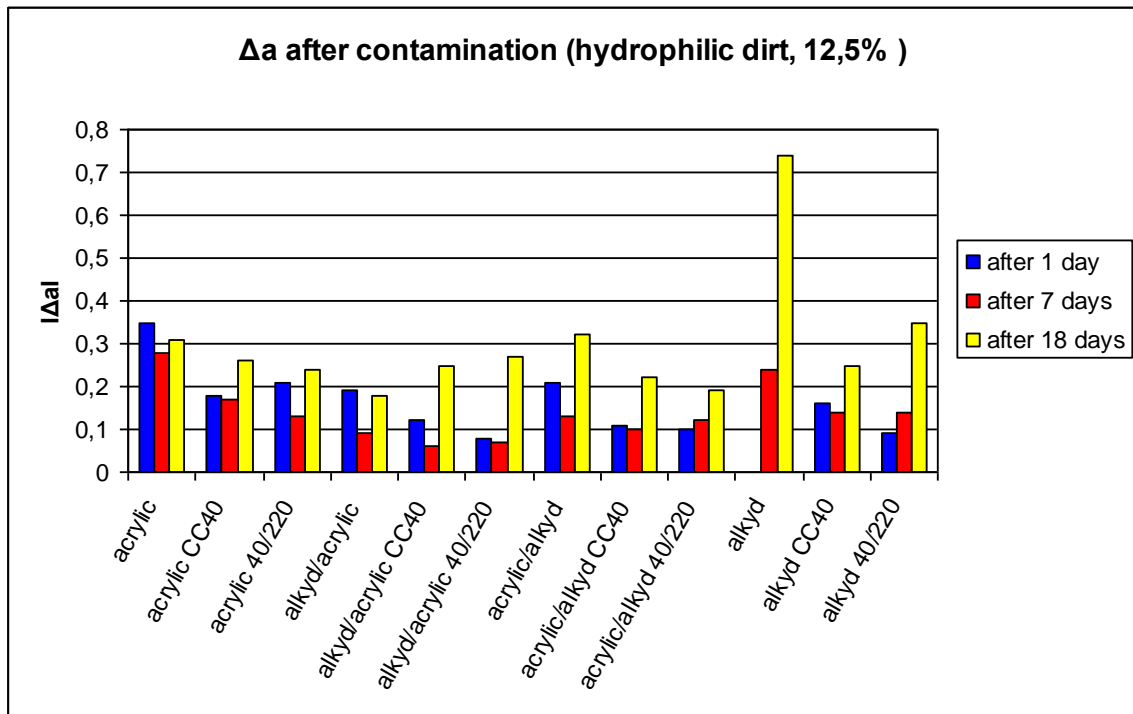


Figure 14: absolute Δa values of cure time dependent contamination with “hydrophilic dirt”

8.2 Results of the heated contamination (12,5wt% Bindzil)

8.2.1 Results of the heated contamination with hydrophobic dirt

All dispersions with the silica show a higher soiling resistance, after each cycle, than the corresponding tinting base. The addition of silica improves the resistance and the acrylate paint (“Bestå”) shows the strongest effect. The improvement of the acrylate paint with CC40 is 52% and with 40/220 it is 62% after the 3.cycle. The silica has the smallest effect on the alkyd paint (“Exponyl”). The ΔL value after rinsing is not displayed because it has almost no effect and the dirt stays on the sample.

Ranking of the dispersions:

1. acrylate 40/220
2. acrylate/alkyd 40/220
3. acrylate CC40
4. alkyd/acrylate 40/220
5. acrylate/alkyd CC40
6. alkyd 40/220
7. acrylate/alkyd
8. alkyd CC40
9. alkyd
10. alkyd/acrylate CC40
11. acrylate
12. alkyd/acrylate

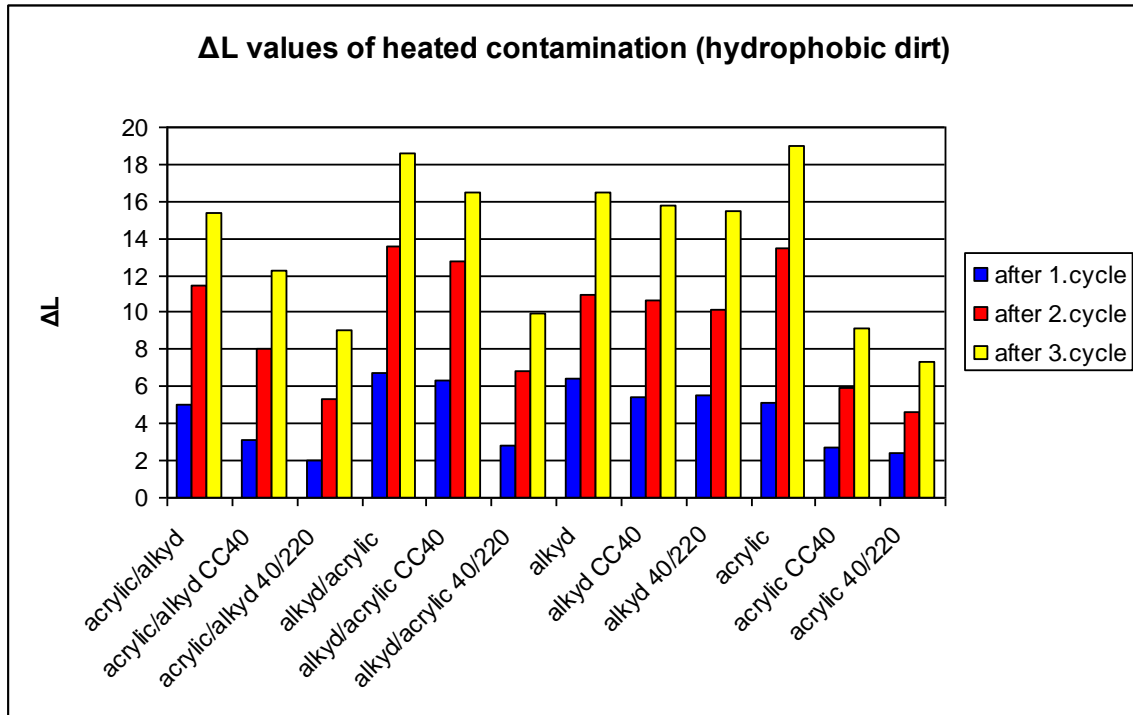


Figure 15: ΔL values after 3 cycles of heated contamination with hydrophobic dirt

8.2.2 Results of the heated contamination with standard dirt

The contamination with standard dirt shows a clear tendency that the dispersions with the silica have a better resistance except the alkyd/acrylate paint CC40 and 40/220 they have a higher dirt pick-up in the beginning and the 40/220 dispersion becomes more resistant after the 2. and 3.cycle. The strongest effect shows the acrylate paint with an improvement of 54% with CC40 and 52% with 40/220 after the 3.cycle. The ΔL value after rinsing is not displayed because it has almost no effect and the dirt stays on the sample.

Ranking of the dispersions:

1. acrylate/alkyd 40/220
2. acrylate/alkyd CC40
3. acrylate CC40
4. acrylate 40/220
5. alkyd/acrylate 40/220
6. alkyd CC40
7. acrylate/alkyd
8. alkyd 40/220
9. alkyd/acrylate
10. alkyd/acrylate CC40
11. alkyd
12. acrylate

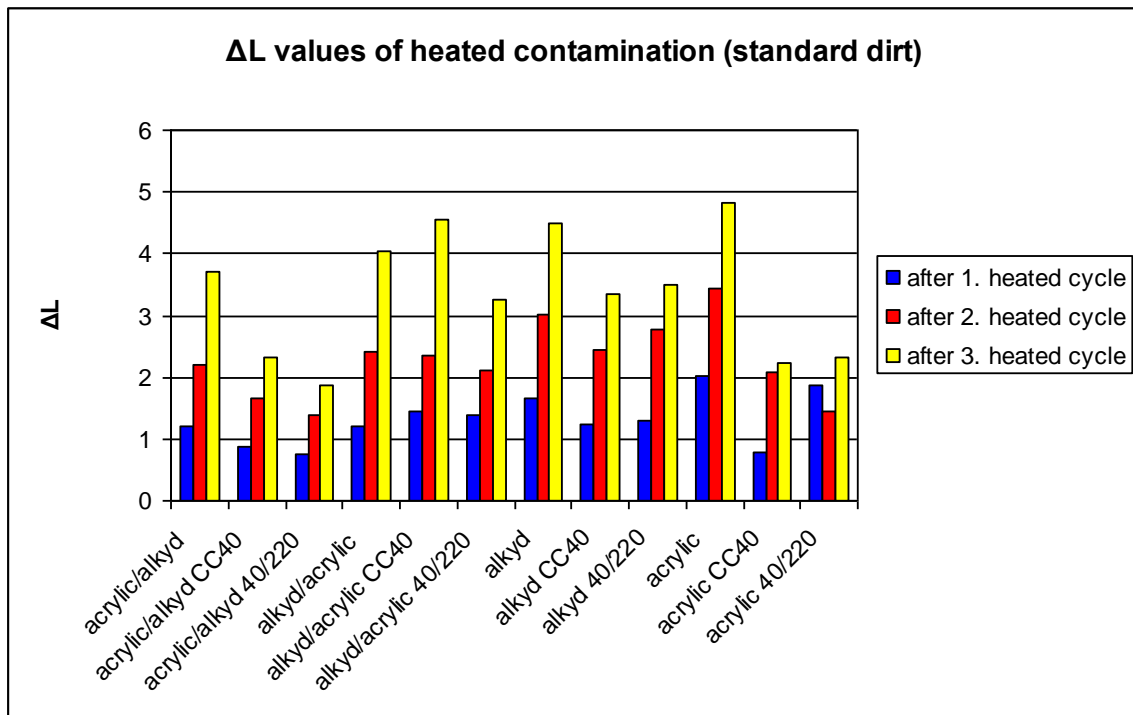


Figure 16: ΔL values after 3 cycles of heated contamination with standard dirt

8.2.3 Results of the heated contamination with hydrophilic dirt

All the dispersions with silica have a higher dirt pick-up resistance after 3.cycles. After the 1.cycle acrylate/alkyd CC40, acrylate/alkyd 40/220 and acrylate CC40 show no difference to the corresponding tinting base, the alkyd CC40 is even worse and the 40/220 shows no improvement as well. After the 2.cycle all dispersions show already a better resistance than the tinting bases. The strongest effect is visible with the acrylate dispersions. The resistance of the CC40 is 79% higher and the 40/220 is 80% higher. The Δa value after rinsing is not displayed because it has almost no effect and the dirt stays on the sample.

Ranking of the dispersions:

1. acrylate 40/220
2. alkyd/acrylate 40/220
3. acrylate/alkyd 40/220
4. acrylate CC40
5. acrylate/alkyd CC40
6. alkyd/acrylate CC40
7. alkyd 40/220
8. acrylate/alkyd
9. alkyd/acrylate
10. alkyd CC40
11. acrylate
12. alkyd

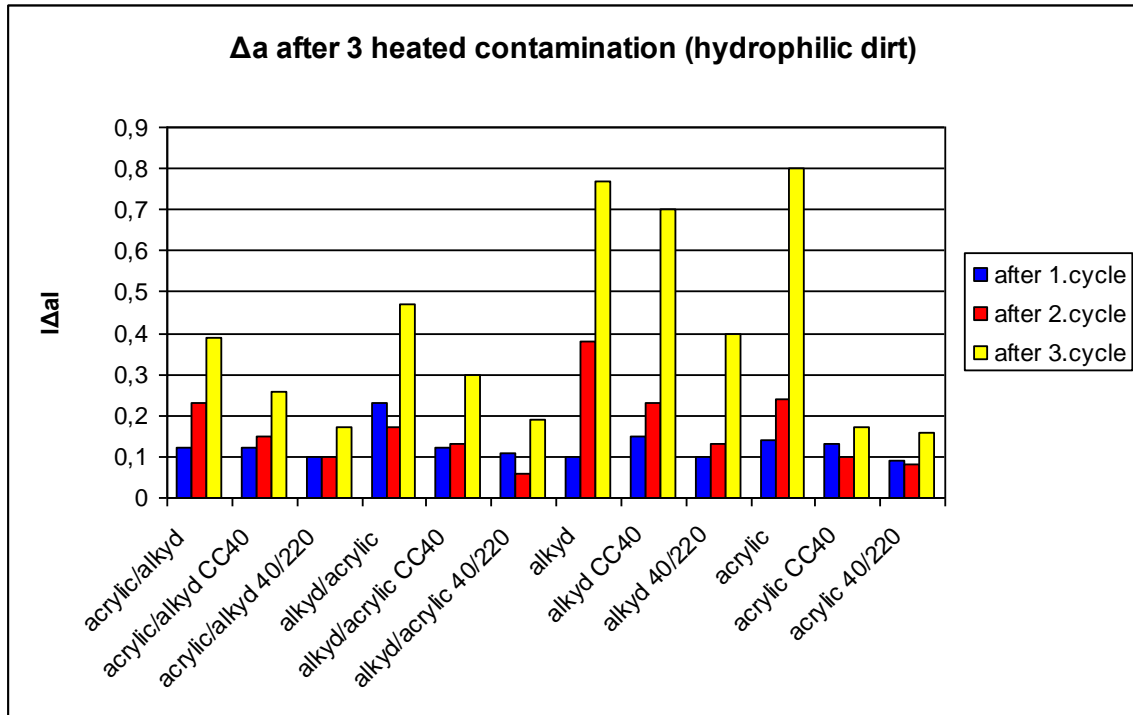


Figure 17: absolute Δa values after 3 cycles of heated contamination with hydrophilic dirt

8.3 Results of heated contamination with different Bindzil concentrations (12.5/ 6/ 3 %)

8.3.1 Results: acrylate/alkyd “Trähusfärg”

8.3.1.1 Results: acrylate/alkyd “Trähusfärg” with hydrophobic dirt

The lowest dirt pick-up, after the 3rd cycle, has the 6% dispersion of 40/220 followed by the CC40. The 12.5% dispersion of the 40/220 shows the next best result after the 6% dispersions. The 3% dispersions have almost the same dirt resistance like the 12.5% CC40 dispersion.

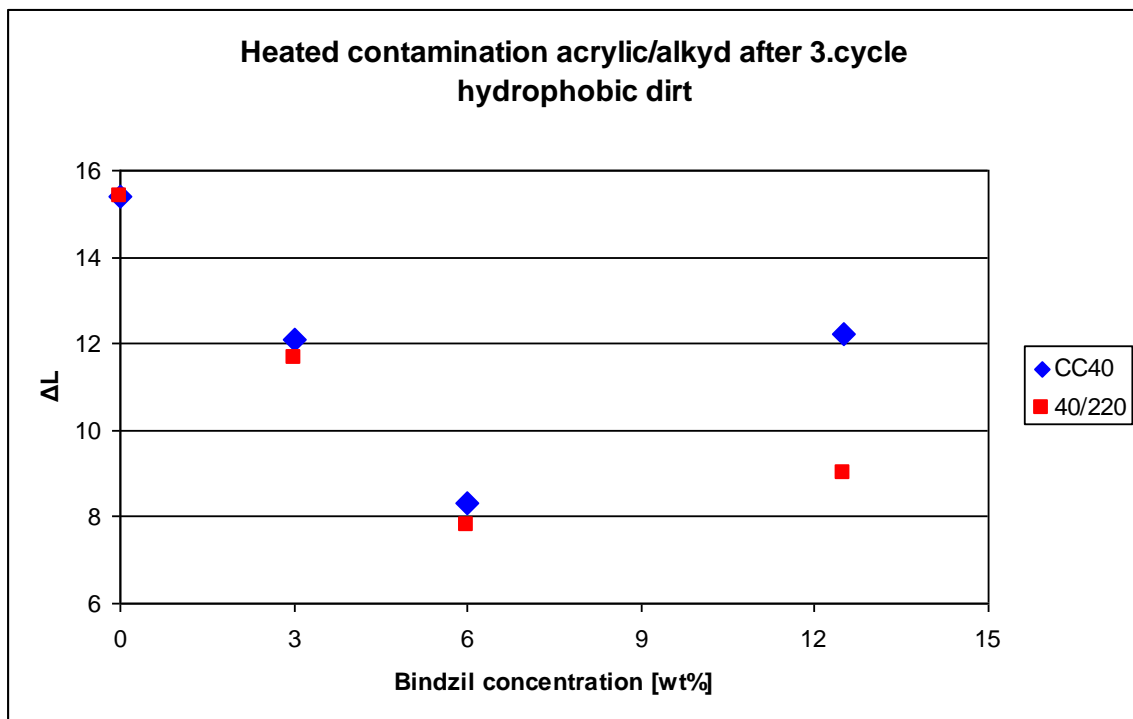


Figure 18: ΔL values after 3rd cycle of heated contamination with hydrophobic dirt and concentrations of 12.5/ 6/ 3% of Bindzil

8.3.1.2 Results: acrylate/alkyd “Trähusfärg” with standard dirt

The lowest dirt pick-up, after the 3rd cycle, has the 12.5% dispersion of 40/220 followed by the CC40. The 3% dispersion of the 40/220 shows the next best result after the 12.5% dispersions.

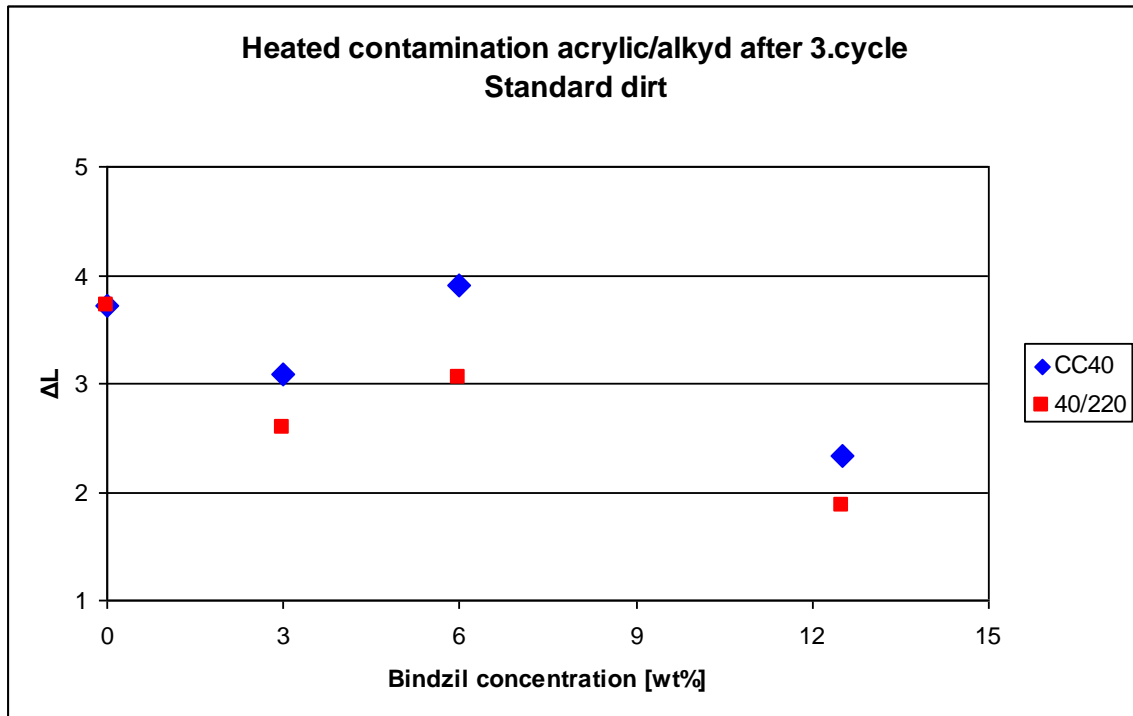


Figure 19: ΔL values after 3rd cycle of heated contamination with standard dirt and concentrations of 12.5/ 6/ 3% of Bindzil

8.3.1.3 Results: acrylate/alkyd “Trähufärg” with hydrophilic dirt

The lowest dirt pick-up, after the 3rd cycle, has the 12.5% dispersion of 40/220 followed by the CC40. The 6% dispersions show the next best result after the 12.5% dispersions. All dispersions with silica show a better resistance than without except the 3% dispersions are even worse than the tinting base.

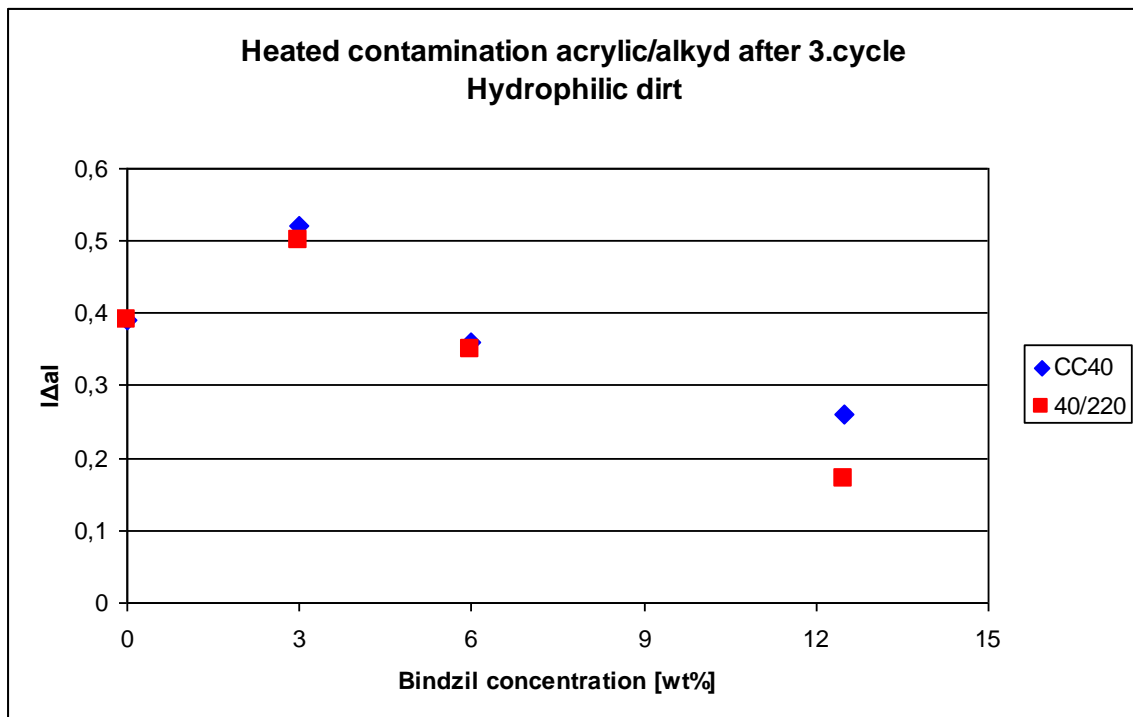


Figure 20: Absolute Δa values after 3rd cycle of heated contamination with hydrophilic dirt and concentrations of 12.5/ 6/ 3% of Bindzil

8.3.2 Results: alkyd/acrylate “Fönsterfärg”

8.3.2.1 Results: alkyd/acrylate “Fönsterfärg” with hydrophobic dirt

The soiling resistance of all dispersions with silica is better than the resistance of the tinting base. The lowest dirt pick-up, after the 3rd cycle, has the 12.5% dispersion of 40/220 followed by the 6% dispersions which show the next best result after the 12.5% dispersion.

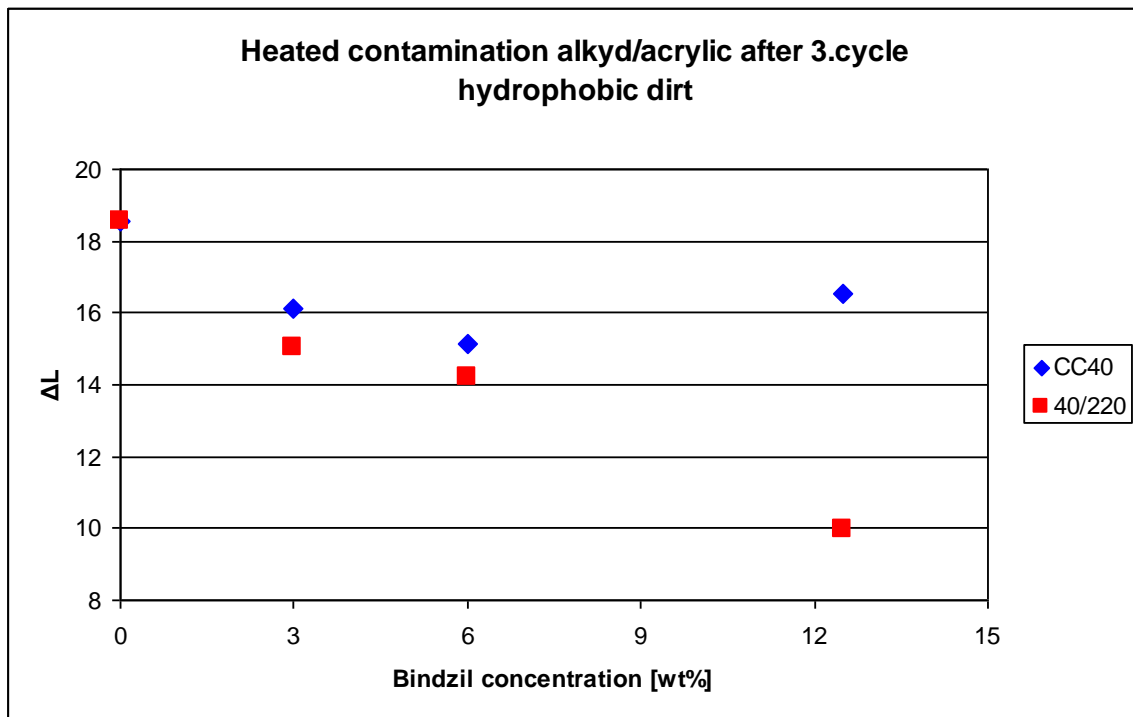


Figure 21: ΔL values after 3rd cycle of heated contamination with hydrophobic dirt and concentrations of 12.5/ 6/ 3% of Bindzil

8.3.2.2 Results: alkyd/acrylate “Fönsterfärg” with standard dirt

The lowest dirt pick-up, after the 3rd cycle, has the 12.5% dispersion of 40/220 followed by the 6% dispersions which show the next best results after the 12.5% dispersion. The 3% dispersions and the 12.5% CC40 show a worse soiling resistance than the tinting base.

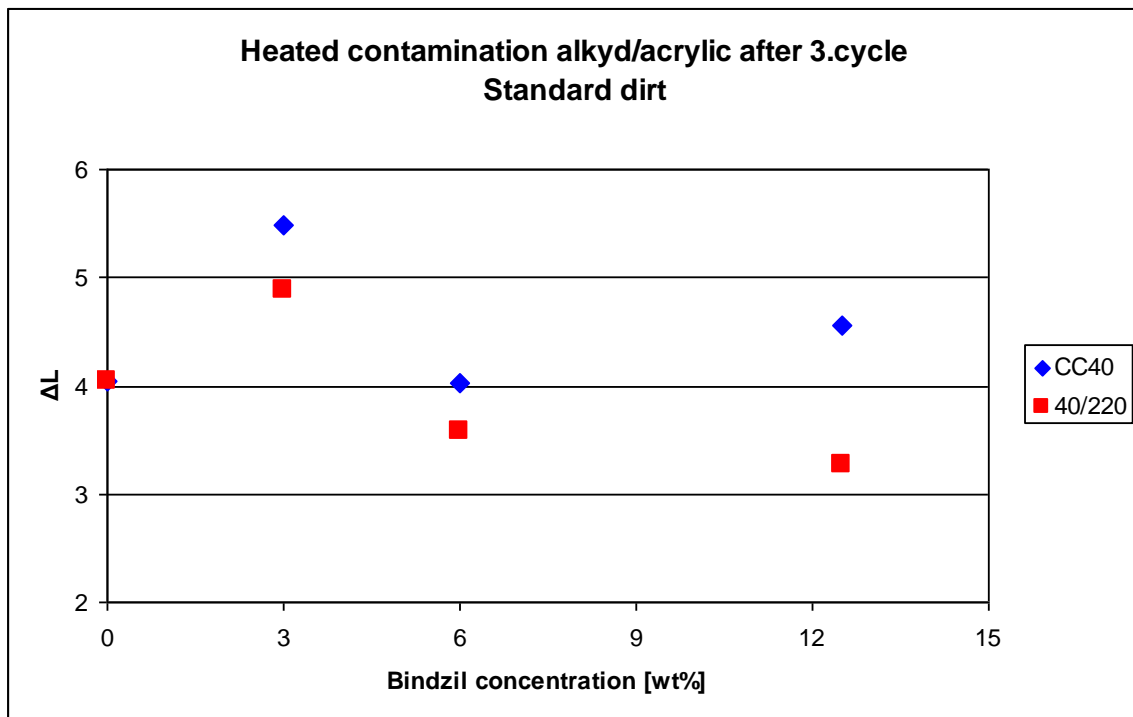


Figure 22: ΔL values after 3rd cycle of heated contamination with standard dirt and concentrations of 12.5/ 6/ 3% of Bindzil

8.3.2.3 Results: alkyd/acrylate “Fönsterfärg” with hydrophilic dirt

The lowest dirt pick-up, after the 3rd cycle, has the 12.5% dispersion of 40/220 followed by the 6% dispersions which show the next best result after the 12.5% dispersion. The 3% dispersions and the 12.5% CC40 show a worse soiling resistance than the tinting base.

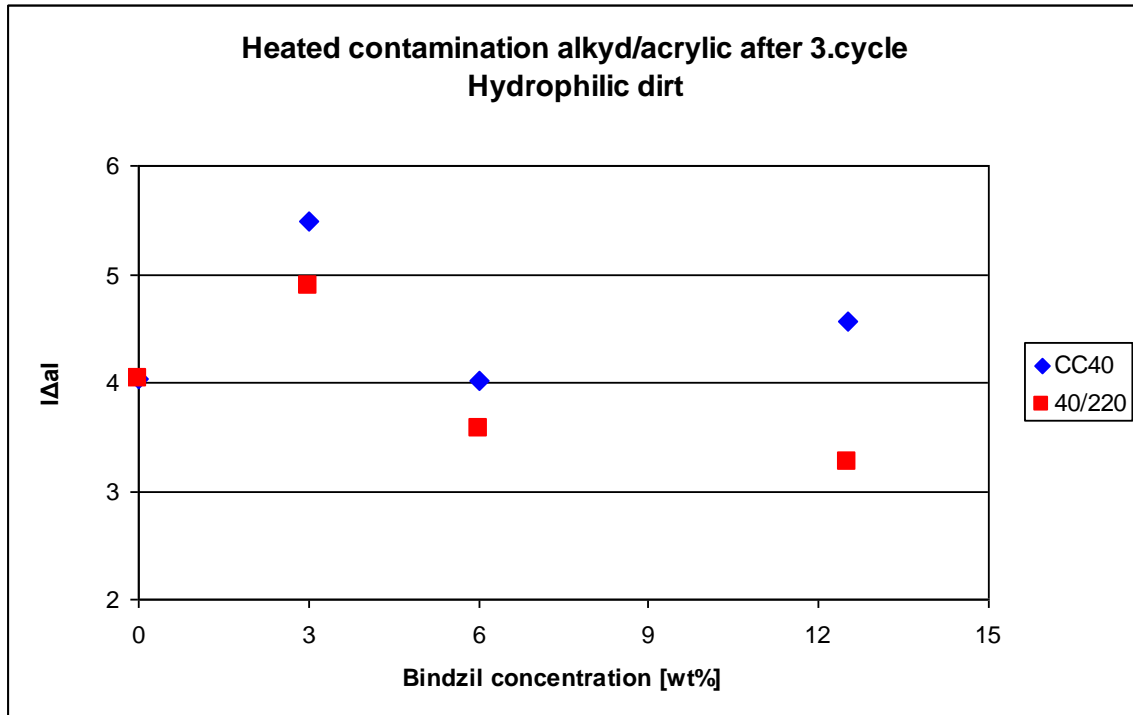


Figure 23: Absolute Δa values after 3rd cycle of heated contamination with hydrophilic dirt and concentrations of 12.5/ 6/ 3% of Bindzil

8.3.3 Results: alkyd “Exponyl”

8.3.3.1 Results: alkyd “Exponyl” with hydrophobic dirt

The lowest dirt pick-up, after the 3rd cycle, has the 6% dispersion of 40/220 followed by the CC40. The 3% dispersion of the 40/220 shows the next best result after the 6% dispersions. The 12.5% dispersions are very similar to the result of the 3% 40/220. The 3% CC40 dispersion is even worse than the tinting base.

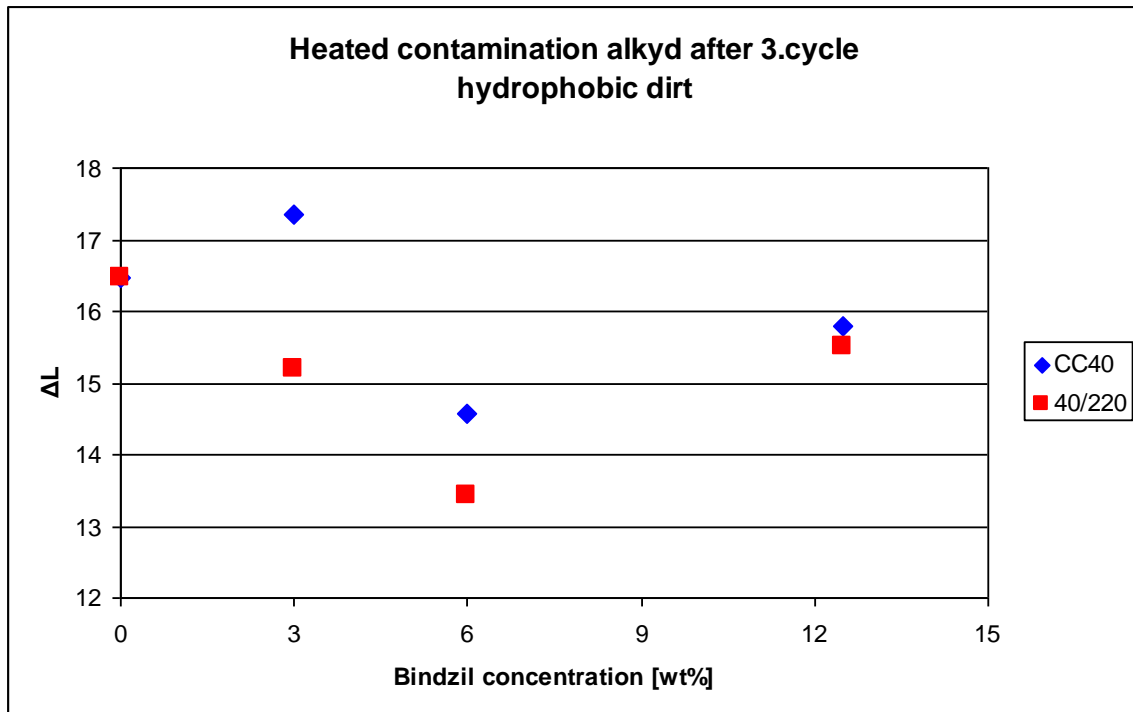


Figure 24: ΔL values after 3rd cycle of heated contamination with hydrophobic dirt and concentrations of 12.5/ 6/ 3% of Bindzil

8.3.3.2 Results: alkyd “Exponyl” with standard dirt

The lowest dirt pick-up, after the 3rd cycle, has the 12.5% dispersion of CC40 followed by the CC40. The 6% dispersions show the next best result after the 12.5% dispersions. The 3% dispersions show a worse soiling resistance than the tinting base.

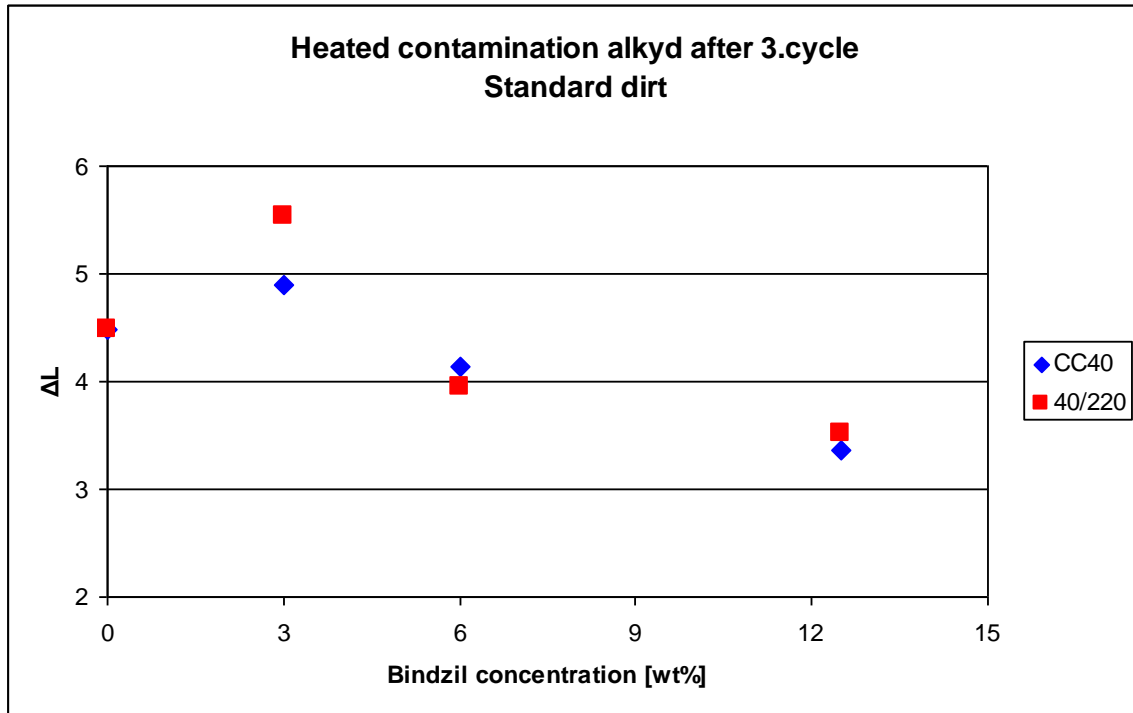


Figure 25: ΔL values after 3rd cycle of heated contamination with standard dirt and concentrations of 12.5/ 6/ 3% of Bindzil

8.3.3.3 Results: alkyd “Exponyl” with standard dirt

The lowest dirt pick-up, after the 3rd cycle, has the 12.5% dispersion of 40/220 followed by the 6% CC40. The next best results are the 12.5% CC40 and 6% 40/220 which are very similar. The 3% dispersions have a lower dirt pick-up resistance than the tinting base.

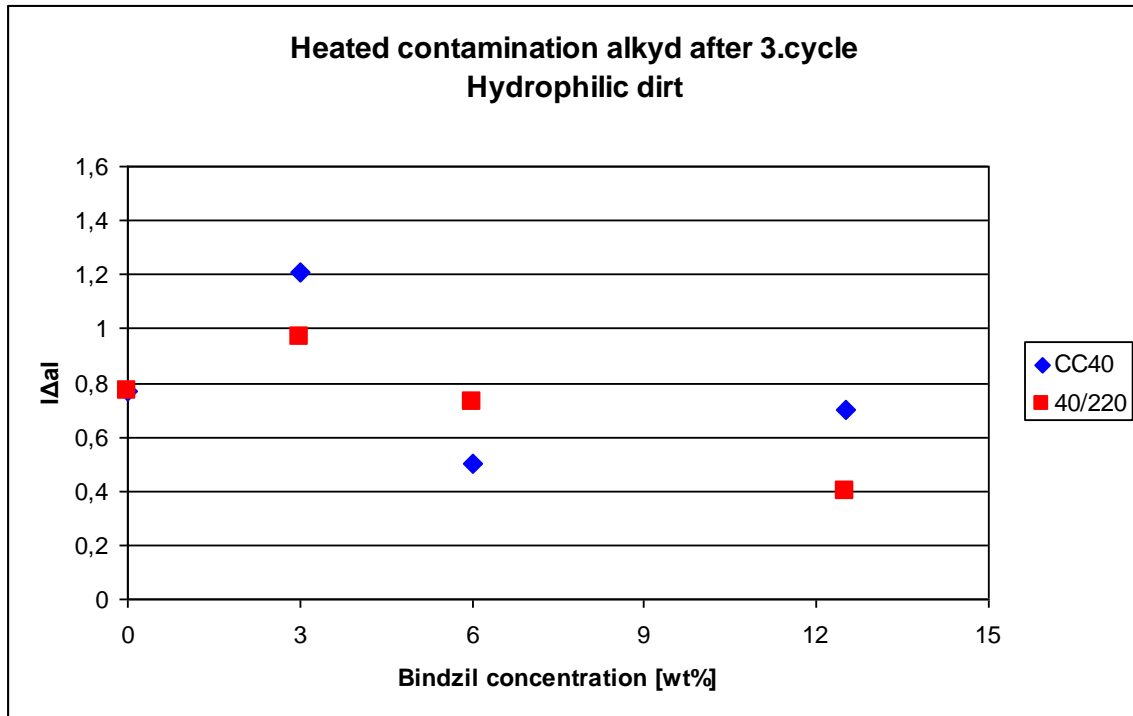


Figure 26: Absolute Δa values after 3rd cycle of heated contamination with hydrophilic dirt and concentrations of 12.5/ 6/ 3% of Bindzil

8.3.4 Results: acrylate “Bestå”

8.3.4.1 Results: acrylate “Bestå” with hydrophobic dirt

The lowest dirt pick-up, after the 3rd cycle, has the 12.5% dispersion of 40/220 followed by the CC40. The 6% dispersions show the next best result after the 12.5% dispersions. The 3% CC40 dispersion shows no improvement to the tinting base.

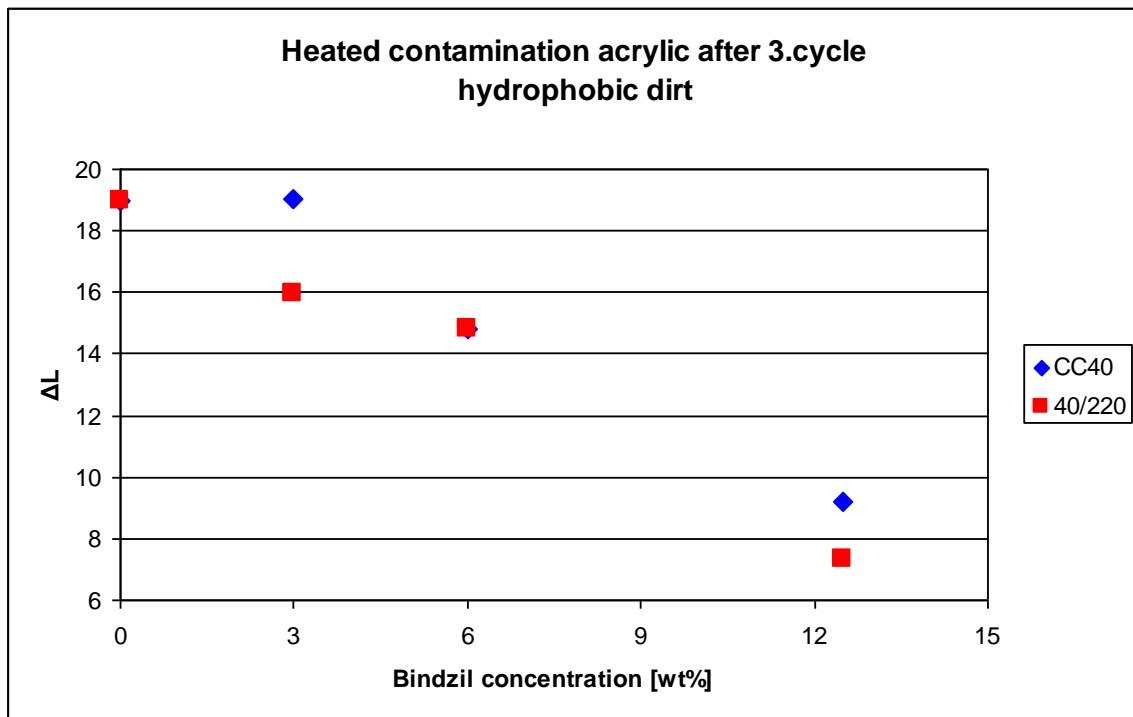


Figure 27: ΔL values after 3rd cycle of heated contamination with hydrophobic dirt and concentrations of 12.5/ 6/ 3% of Bindzil

8.3.4.2 Results: acrylate “Bestå” with standard dirt

The lowest dirt pick-up, after the 3rd cycle, has the 12.5% dispersion of CC40 followed very closely by the 40/220. The other dispersions with 3% and 6% show very similar results compared to each other and they all show a worse soiling resistance than the corresponding tinting base.

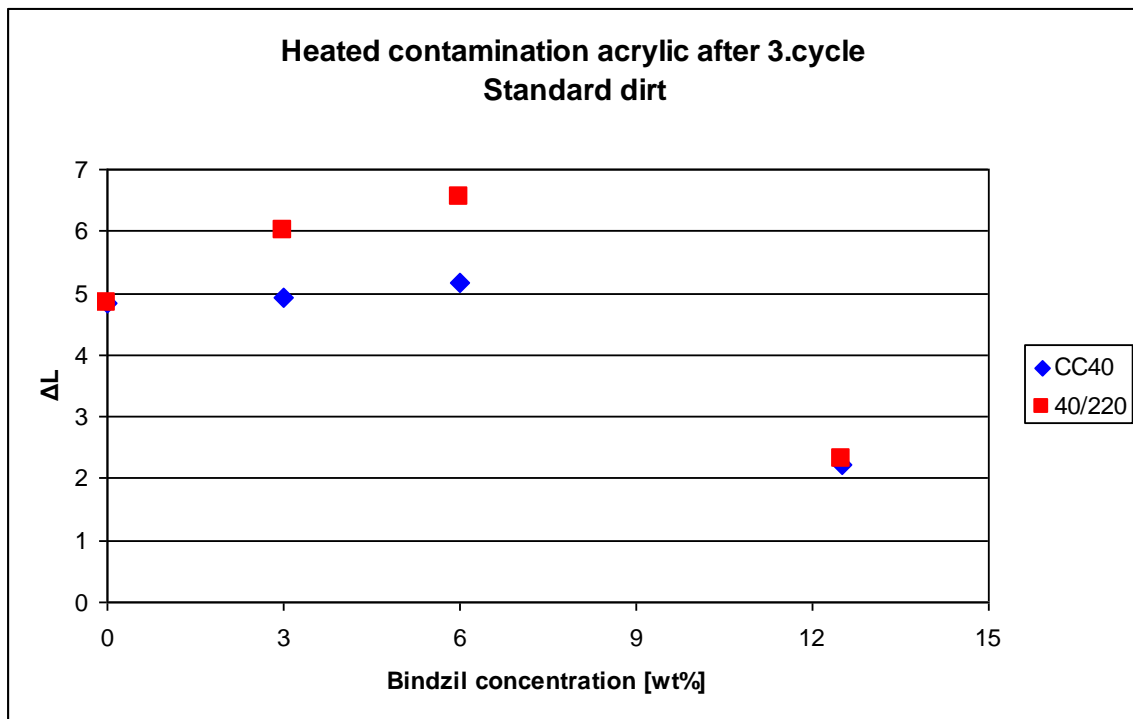


Figure 28: ΔL values after 3rd cycle of heated contamination with standard dirt and concentrations of 12.5/ 6/ 3% of Bindzil

8.3.4.3 Results: acrylate “Bestå” with hydrophilic dirt

All dispersions show a better soiling resistance than the corresponding tinting base. The lowest dirt pick-up, after the 3rd cycle, has the 12.5% dispersion of 40/220 followed very closely by the CC40. The 6% dispersions show the next best result after the 12.5% dispersions.

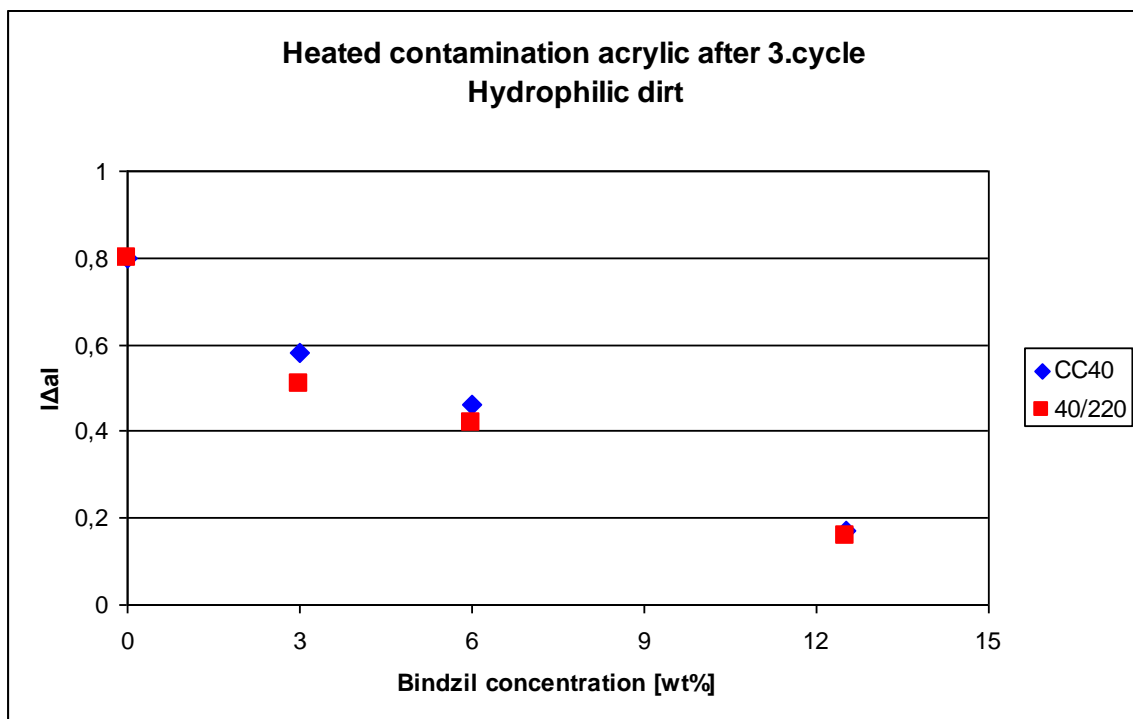


Figure 29: Absolute Δa values after 3rd cycle of heated contamination with hydrophilic dirt and concentrations of 12.5/ 6/ 3% of Bindzil

9 Discussion

9.1 Indoor testing methods

At first the method with different curing times was used to determine the dirt pick-up resistance but it took a long time before the samples could be measured and the effect of the thermoplasticity during heat exposure cannot be seen. With the cure time method it is possible to see tendencies of the dispersions with silica nanoparticles but with the method of heated contamination the tendencies are clearer. Furthermore the effect that silica increases the coating surface hardness [1] which leads to less flow of the coating during heat exposure (e.g. sunlight), is visible. The results with the heated contamination are clearer because of the stronger whiteness change caused by a higher dirt pick-up. A higher temperature gives a higher tackiness of thermoplastic materials such as architectural coatings and these materials have a higher dirt pick-up.

9.2 Exponyl (alkyd)

The silica nanoparticles have not such a big effect on the hardness of the alkyd paint “Exponyl” even with a high concentration of 25%wt. of silica dispersion. The hardness increases but just with 29% for the 40/220 and 43% for the surface modified type CC40. In this case it seems the alkyd responds better to the more hydrophobic type of silica nanoparticles.

The rheology is not drastically affected by the silica because the main rheological properties were not changed. The CC40 dispersions were easier to handle because the CC40 had a stronger thinning effect on the dispersions compared with the 40/220 which showed a stronger thickening effect on the viscosity. With a concentration of 25% wt. it was difficult or almost impossible to apply the 40/220 paint properly with the applicator.

The CC40 showed a stronger phase separation than the 40/220 but it could be easily homogenized again by stirring.

The early dirt pick-up test showed a tendency that the silica nanoparticles improve the early dirt pick-up resistance. After 2h of curing the 40/200 shows a 93% higher resistance than the tinting base. After 24h of curing it is still around 90%. The CC40 result is better than the result of the tinting as well but not that good as the 40/220. After 2h the dirt pick-up is 56% less than the soiling of the tinting base and after 24h it is almost like the tinting base. After 30 days of curing the paints showed enormous high values for the CC40 and 40/220 which can be caused by a rearrangement of the surface but it is hard to tell because it bargains for a multiparticle system and you cannot exactly tell what caused this phenomenon. What may indicates that the rearrangement is going on, is the tendency that the dirt pick-up is getting higher with a longer cure time.

The tests of the dependency on the cure time showed that a longer cure time of the alkyd paint leads to a higher resistance with both types of silica in the first 7 days. After 18 days of curing the same effect occurred, like at the early dirt pick-up test, that the dispersions with silica were no longer more dirt pick-up resistant than the tinting base and the silica was no longer effective and it may has no more effect on the hardness.

The 40/220 showed a lower change in the brightness when hydrophobic dirt was used but the CC40 was more effective even after 18 days and was more resistant than the tinting base. The CC40 showed better results as well with hydrophilic dirt.

The heated contamination with hydrophobic dirt showed clearer results than the cure time dependent method but the results were quite similar to the results of the cure time dependent method. The difference was the time it took to get the testing done, it was much faster to obtain the results with the new method. With standard dirt the result was different, both types of Bindzil showed a higher resistance than the tinting base. The CC40 showed a little better result than the 40/220 but with hydrophilic dirt the result with 40/220 was much better than the CC40. In general the 40/220 seems to have a better

effect on the dirt pick-up resistance. All the dispersion with silica showed a better dirt pick-up resistance against all three types of dirt compared with the tinting base.

For the testing with different concentrations of silica the heated contamination method was used and it showed the tendency that the dirt pick-up resistance increases, as expected, with a higher amount of silica. In general the 40/220 showed with alkyd paint a better resistance against hydrophobic and hydrophilic dirt than the CC40. The CC40 showed the tendency that it is more effective against standard dirt.

9.3 Fönsterfärg (alkyd/acrylate)

The silica nanoparticles have a quite good effect on the hardness of the alkyd/acrylate paint “Fönsterfärg” even with a concentration of 12.5%wt. of silica dispersion. The hardness increases with 39% for the 40/220 (12.5%) and 75% (25% wt.) for the surface modified type CC40. In this case it seems the alkyd/ acrylate system responds better to the silica nanoparticles than the alkyd paint.

The rheology is not drastically affected by the addition of the silica because the main rheological properties were not changed.

The results of the cure time related tests point to that the 40/220 type has better effect on the paint than the CC40.

With the heated contamination it was even more obvious that the 40/220 has a much better resistance with every type of dirt than the CC40 and the tinting base. In general the dispersions with silica have a higher resistance against hydrophobic and hydrophilic dirt compared to the tinting base. With standard dirt the resistance of the tinting base was higher after the first cycle than the resistance of the both silica dispersions. The 40/220 became more resistant with a higher contamination after the 2.cycle. than the tinting base and the CC40, which has a lower resistance than the tinting base against standard dirt.

The testing with different concentrations of silica showed the tendency that the dirt pick-up resistance increases, as expected, with a higher amount of silica. In general the 40/220 showed a better resistance against all different types of dirt than the CC40 type.

9.4 Trähusfärg (acrylate/alkyd)

Both types of silica have a really strong effect on the hardness even with a concentration of 12.5wt% with 40/220. The hardness of the film increased for 79%.

The rheology is not drastically affected by the addition of the silica and the dispersions keep their main rheological properties.

The cure time dependent tests showed that the acrylate/alkyd 40/220 paint has the best resistance of all paints against hydrophilic and hydrophobic dirt. The CC40 dispersions have a little less good resistance but they are still one of the most effective paints against dirt pick-up. It seems that the acrylate/alkyd based system responds very good to the addition of silica nanoparticles.

With the heated contamination the acrylate/alkyd paints showed really good results again. The 40/220 dispersion is more effective against hydrophobic dirt than the CC40 which is still quite effective compared to the tinting base. Against standard dirt the acrylate/alkyd based systems were the most effective ones but the 40/220 was still slightly better than CC40. For hydrophilic dirt the 40/220 showed better results than the CC40 as well. In general the 40/220 seems to be more effective against all the different types of dirt than the CC40. All the dispersion with silica showed a higher resistance against all types of dirt compared with the resistance of the tinting base.

The testing with different concentrations of silica showed the tendency that the dirt pick-up resistance increases, as expected, with a higher amount of silica. In general the 40/220 showed a better resistance against all different types of dirt than the CC40 type.

9.5 Bestå (acrylate)

Both types of silica have a strong effect on the hardness even with a concentration of 12.5wt%. The hardness of the film increased for 40% with CC40 and 45% with 40/220. The rheology is not drastically affected by the addition of the silica and the dispersions keep their main rheological properties.

The cure time dependent testing showed that the 40/220 dispersion is one of the most effective paint against hydrophobic dirt and the CC40 showed a good resistance as well

but it was not that good as the 40/220. When hydrophilic dirt was used the 40/220 and the CC40 showed similar results but the resistance with 40/220 was still slightly higher.

With the heated contamination the 40/220 dispersion was the most resistant one against hydrophobic dirt and the CC40 was one of the most resistant ones as well. With standard dirt the two types of silica showed similar results and were both really effective. With hydrophilic dirt the 40/220 paint was the most effective one again and the CC40 showed a good resistance as well.

In general the silica showed the strongest effect with the acrylate paint but the 40/220 seems to be the more effective type than the CC40. All dispersions with silica showed a higher resistance against all types of dirt compared with the resistance of the tinting base. The testing with different concentrations of silica showed the tendency that the dirt pick-up resistance increases, as expected, with a higher amount of silica.

In general the 40/220 showed with acrylate paint a better resistance against hydrophobic and hydrophilic dirt than the CC40 type. It seems that the CC40 shows a better resistance against standard dirt.

10 Summary

- The addition of silica increases the film hardness for all different binders
- The addition of silica has no drastic effect on the rheological properties of the dispersions. In general the CC40 shows more phase separation but the dispersion can be easily homogenized again by stirring.
- Higher dirt pick-up resistance with silica
- The 40/220 Bindzil seems to be more effective with all binders than the surface modified more hydrophobic CC40.
- The 40/220 dispersions seem to be more resistant against all different types of dirt with the paints which are based on combination of binders (alkyd/acrylate or acrylate/alkyd). The CC40 dispersions of the paints which are based on only one binder (alkyd, acrylate) are more effective against standard dirt but against hydrophobic and hydrophilic dirt the 40/220 dispersions are still more effective.
- In general the acrylate based paints seem to respond better to the addition of silica
- It seems that the “early dirt pick-up” resistance can be improved by adding silica to the alkyd paint but it just seems to be effective in the first hours or days after the application of the paint

11 Instruments

Rheometer:

The rheology was measured with the Gemini from “Bohlin Instruments”.

For the rheological measurements a cylindrical system with the following parameters was used:

shear rate: 0.1 – 200 ; 200 – 0.1 [1/s]; time: 281.8 s; temperature: 25°C; 5s delay time

Dispermat:

Dispersing the silica dispersions into the paints was conducted with the “Dispermat” VMA – Getzmann GMBH, Germany. The nanoparticles were dispersed at 3000rpm for 5 minutes.

Colorimeter:

For the color measurements (Lab - values) the X- Rite SP60 was used. 7 measurements were performed on each sample.

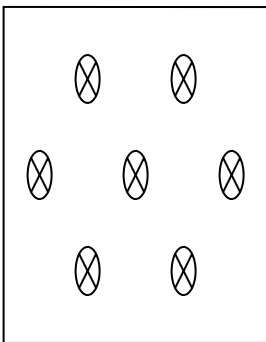


Figure 30: measuring points at the samples

König Pendulum hardness:

The König pendulum hardness was measured with a Erichsen 299 Instrument at 24.6° C and a relative humidity of 45.4 % and glass panels as substrate.

Application

The paints were applied with an Erichsen 9490 applicator with a wet film thickness of 200µm and aluminum sheets as substrate.

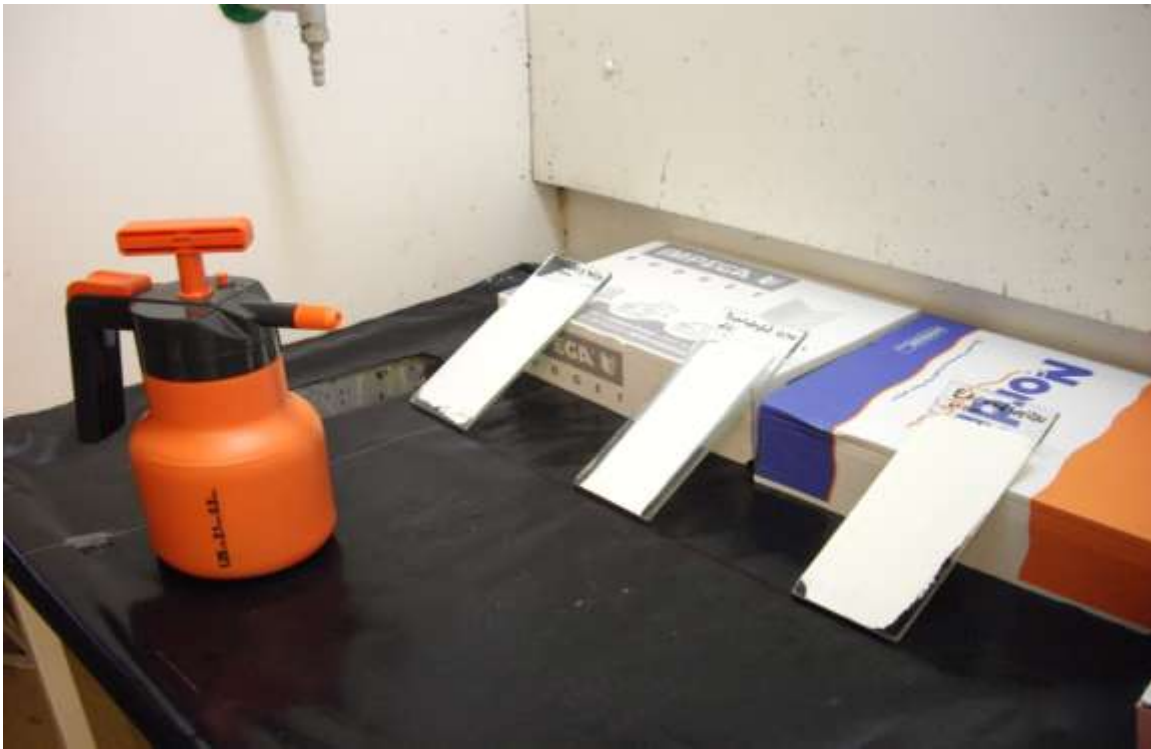
Dirt spraying

The dirt solutions were sprayed with Gardena spraying bottles at the maximal pressure with a distance of 30-40cm to the sample.

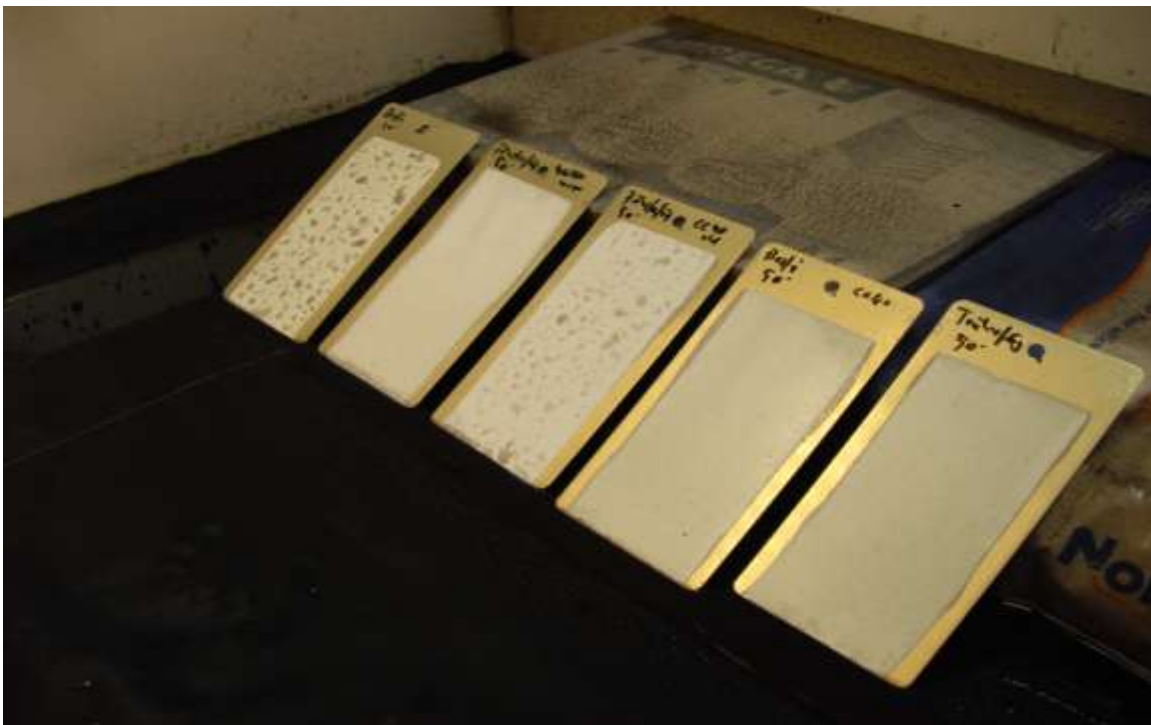
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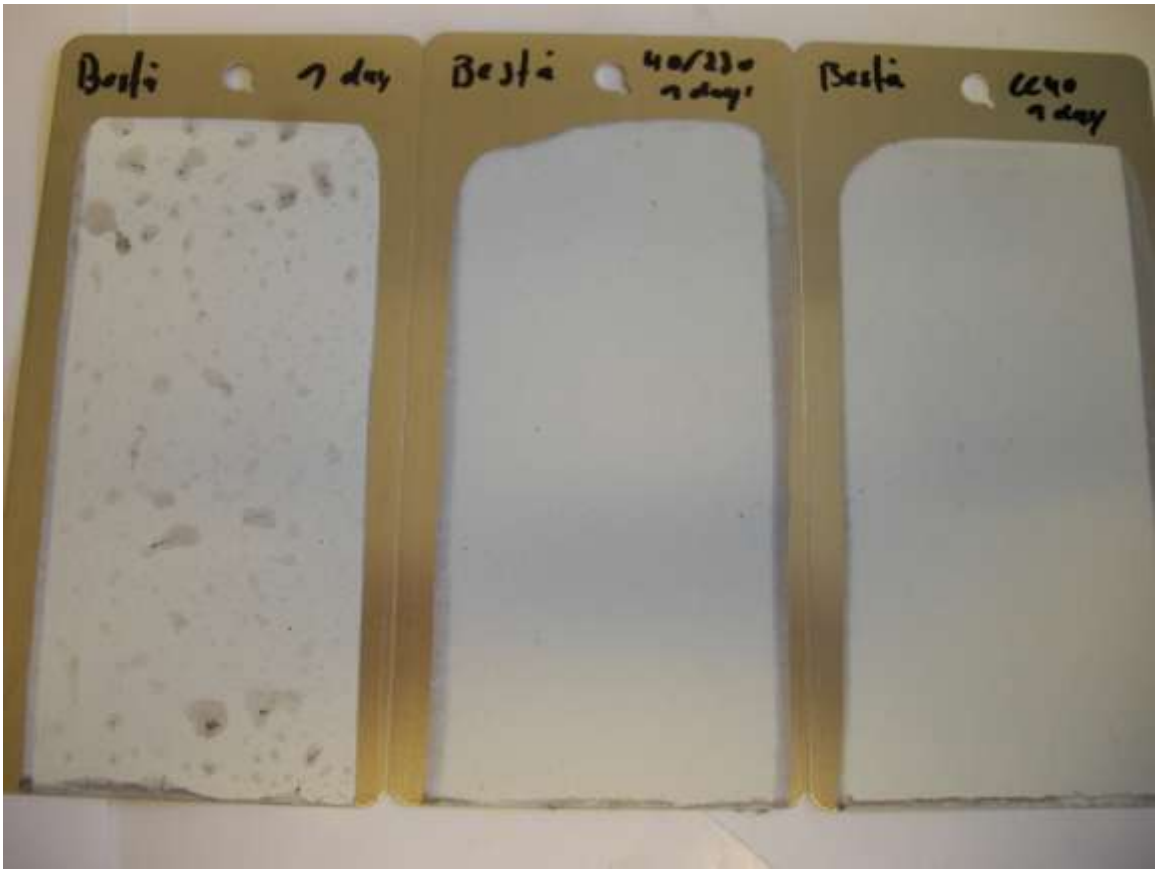
Appendix 1



Dirt spraying



Contaminated samples



Contaminated acrylate samples after contamination and 1 day of curing

Appendix 2

Results from exterior testing

The samples were placed outdoors (Bogesund) in July 2009 and collected in April 2010. All samples should be considered as non-premium products and the evaluation was done after Philipp finished his internship at YKI. We always compare the unmodified paint with paints consisting of 12.5 wt% Bindzil. The results of the study are summarized below based on 7 measurements on each panel and measured on 9 different panels:

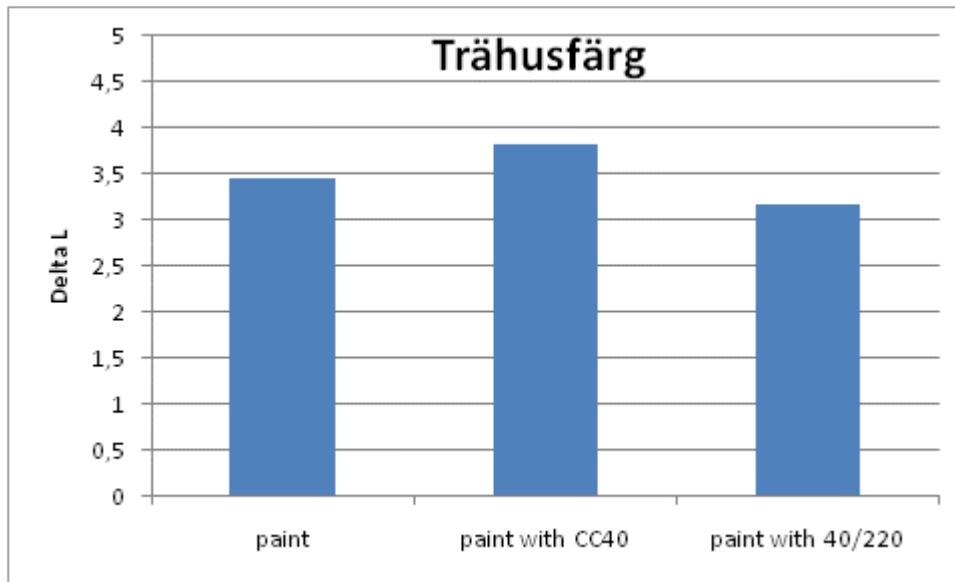
12.1.1 Results: acrylate/alkyd “Trähusfärg”

Photograph of the paints after exposure.



Photographs after 9 month exposure period.

Lightness change ΔL under exposure.



Lightness change under the 9 month exposure period.

It can be seen by eye that the paint with CC40 is darker compared to the other two paints which are difficult separate by eye. We cannot really explain this variation between the samples but note that the trend for “Trähusfärg” is somewhat different from the other paints with regard to the Delta L change (darkening) of the paint with CC40 (see results below). The paint with 40/220 is performing slightly better compared to the unmodified paint. This result is seen more or less strongly in all investigated paints.

Δa change under exposure.

The change in delta a were about -0,1 for all the three formulations. Hence no significant variation was detected.

Δb change under exposure.

The change in delta b were about -1,1 for all three formulations. Hence no significant variation was detected.

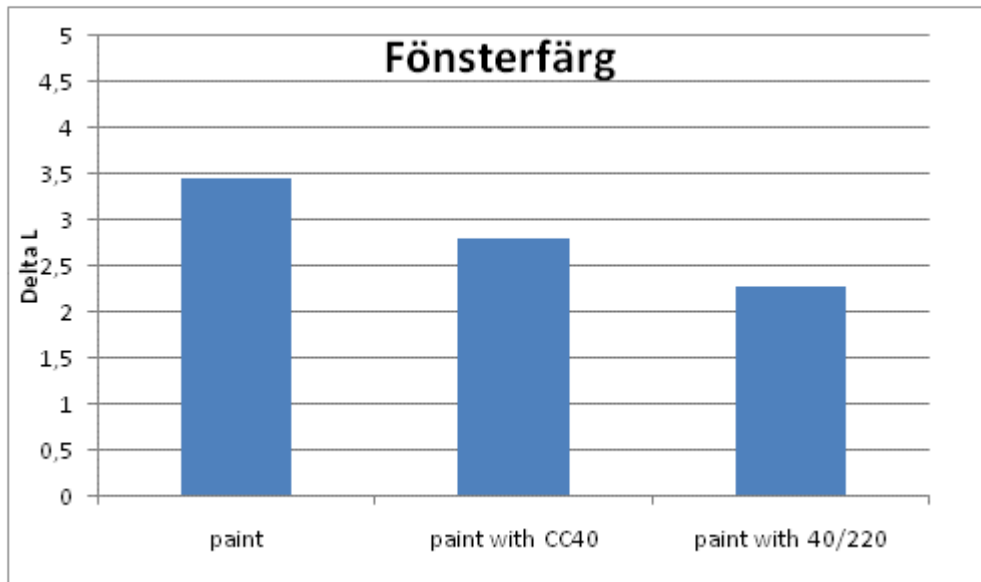
12.1.2 Results: alkyd/acrylate “Fönsterfärg”

Photograph of the paints after exposure.



Photographs after 9 month exposure period.

Lightness change ΔL under exposure.



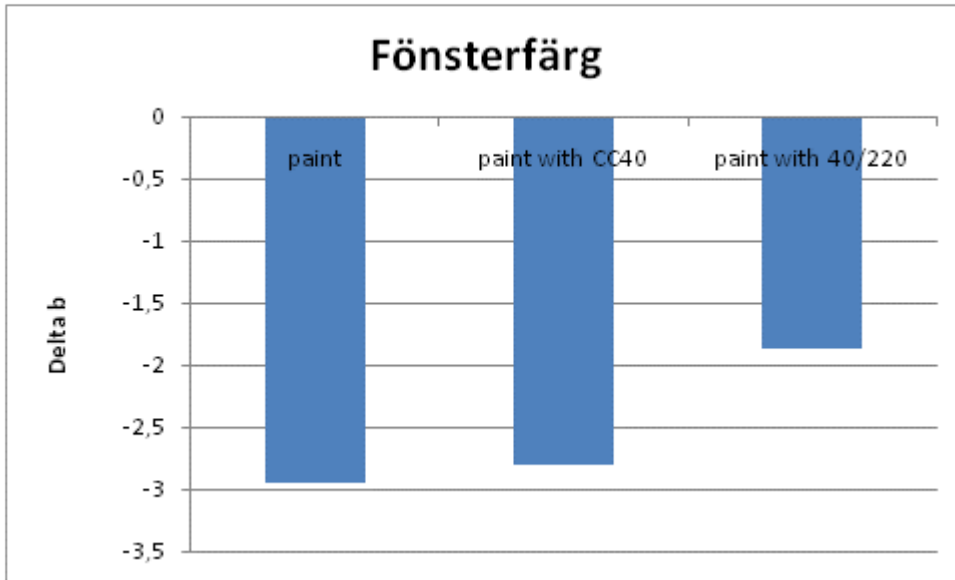
Lightness change under the 9 month exposure period.

The darkening of the unmodified paint "Fönsterfärg" is higher compared to the paints formulated with silica and this is also seen by eye. The paint with 40/220 is performing best followed by the paint with CC40. We speculate that hardening of the paint surface (measured) possibly combined with a decreased water contact angle (not measured but seen in some of the laboratory trials) reduce dirt pickup. The hardening of the paint surface can lead to a smaller mobility of the binder which then has a less change of flowing over dirt anchoring the dirt inside the paint. A decreased water contact angle leads to a better spread of rain water providing a better cleaning of dirt accumulated at the surface.

Δa change under exposure.

The average of delta a is -0,04 for all three paints and this is more or less zero giving no shift in this colour vector.

Δb change under exposure.

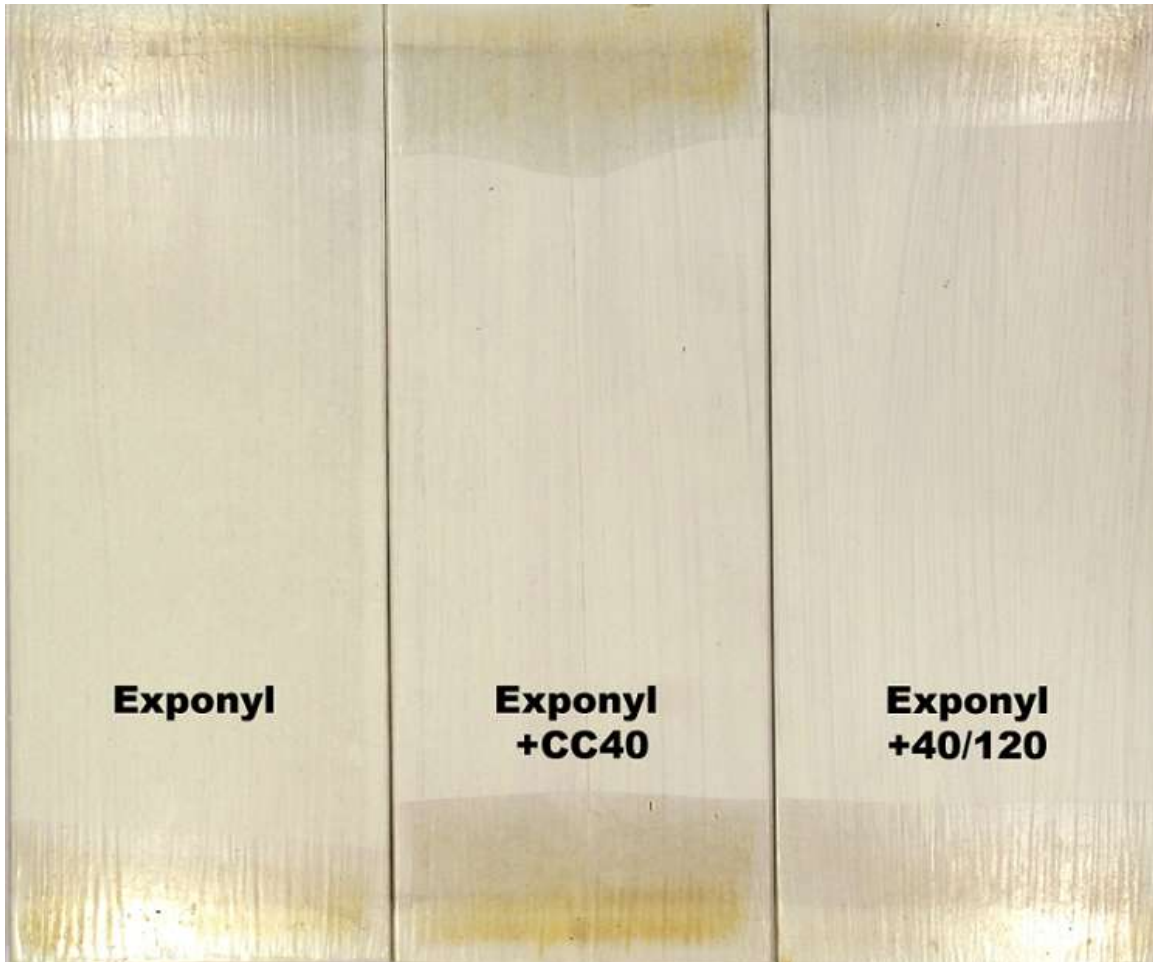


The change in delta b under the 9 month exposure period.

Interestingly we note a much lower blueish shift for the “Fönsterfärg” with 40/220 as compared to the other two paints. We speculate that compounds stemming from the trees around the field station have a lower tendency to attach to paint with 40/220 possibly due to a decreased tackiness of this paint.

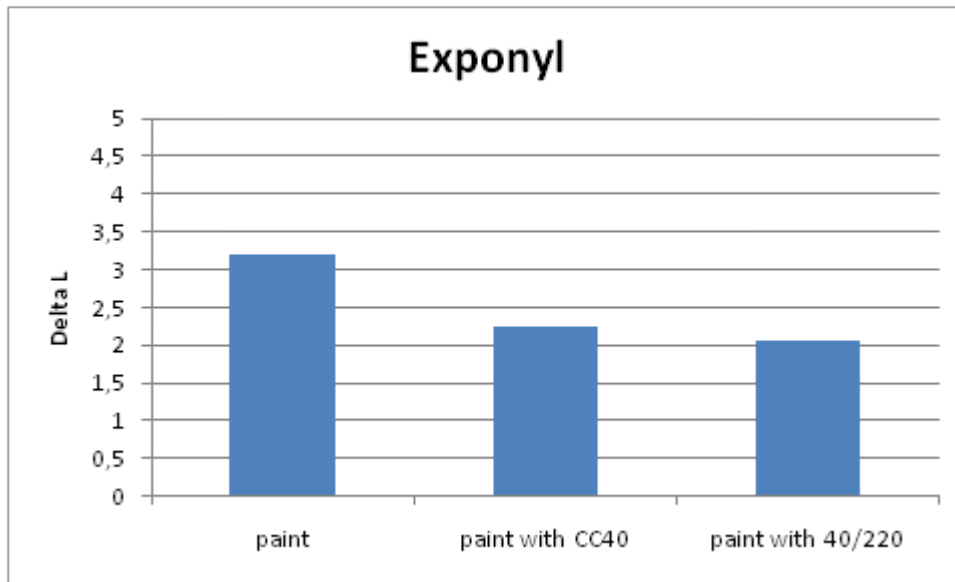
12.1.3 Results: alkyd “Exponyl”

Photograph of the paints after exposure.



Photographs after 9 month exposure period.

Lightness change ΔL under exposure.



Lightness change under the 9 month exposure period.

The alkyd paint with silica has an increase in lightness with about 2 while the unmodified paint has a lightness change over 3. This effect can clearly be seen on the panels. Alkyd resins are polymerizing after application. It is therefore important to keep in mind how and where the paint has been applied on the panels since the tackiness is reduced substantially after a few days of drying. In this test the panels were prepared in the laboratory a few days before being placed outside. Repainting at home would be done directly on the panels outdoors and it is very likely that the difference in early dirt pickup can be larger as compared to the data generated in this study.

Δa change under exposure.

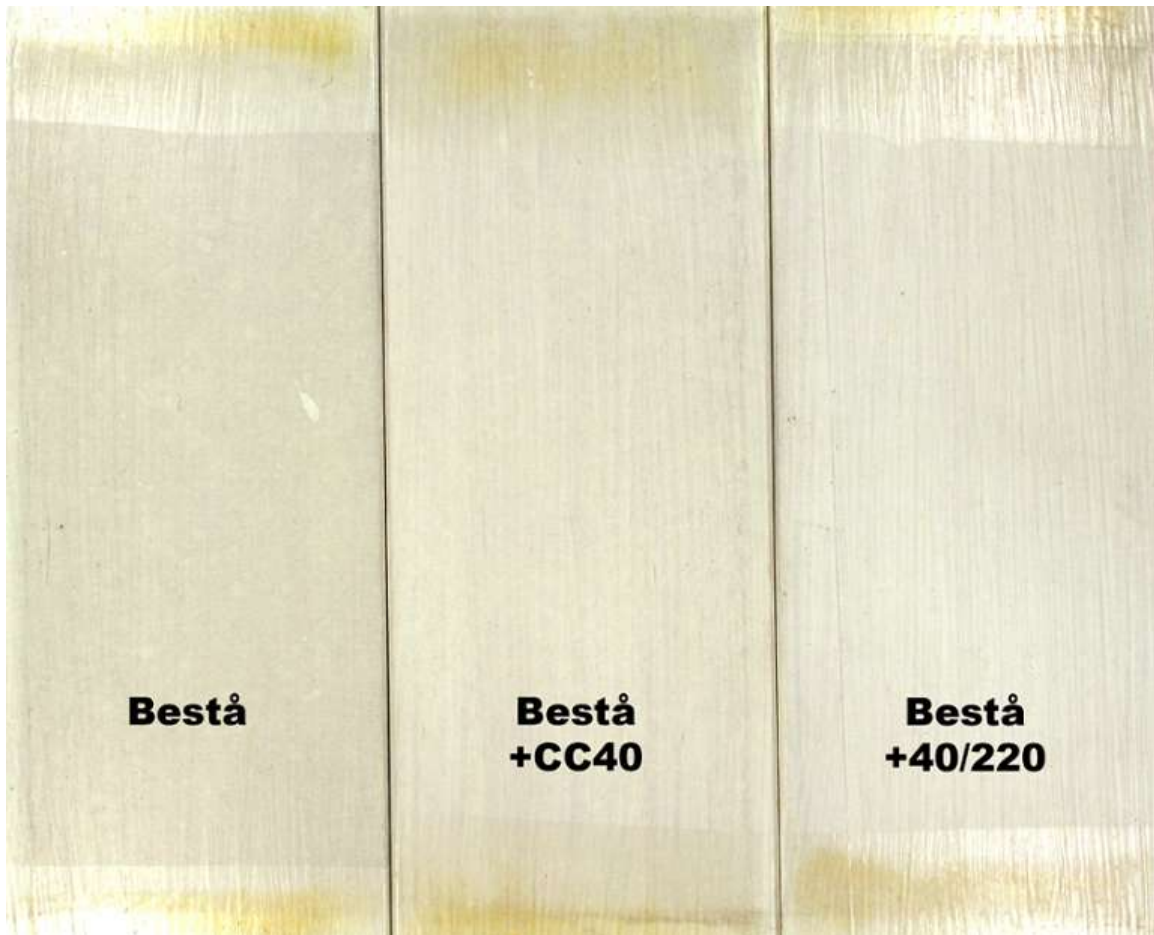
The paints has on average a change of -0,14 which is close to zero meaning no significant shift on this paint vector.

Δb change under exposure.

The small differences around zero in this paint vector are regarded as insignificant.

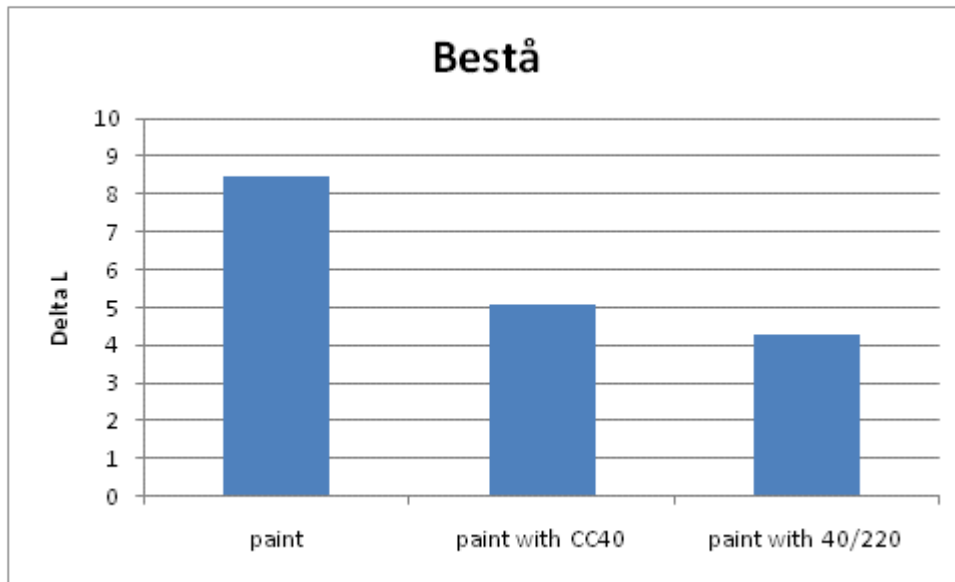
12.1.4 Results: acrylate “Bestå”

Photograph of the paints after exposure.



Photographs after 9 month exposure period.

Lightness change ΔL under exposure.



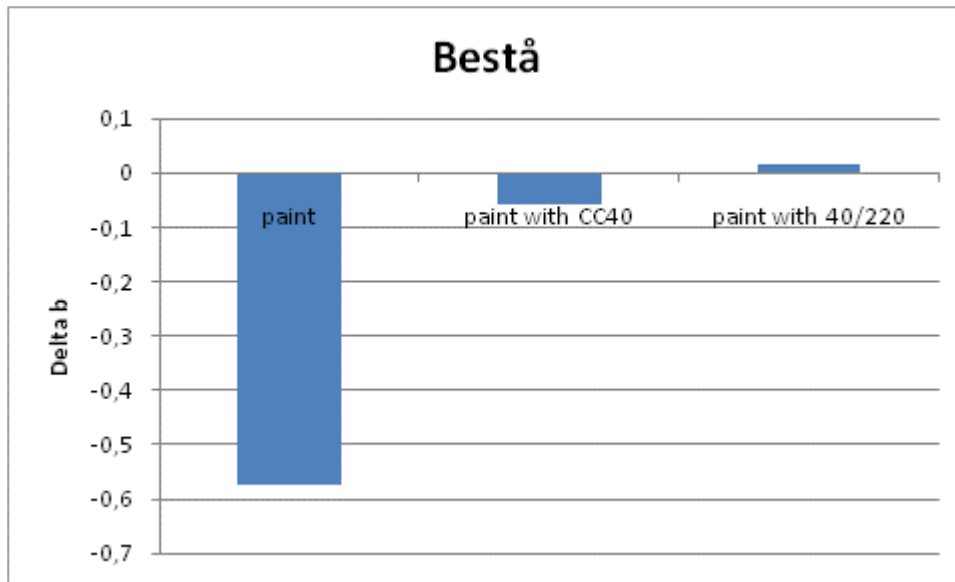
Lightness change under the 9 month exposure period.

The paint “Bestå” became more than 8 lightness units darker during the time of exposure. The paint with CC40 increased with 5 units and the paint with 40/220 with about 4 units. The difference is clearly visible by eye. We speculate that hardening of the paint surface (measured) possibly combined with a decreased water contact angle (not measured but seen in some of the laboratory trials) reduce dirt pickup. The hardening of the paint surface can lead to a smaller mobility of the binder which then has a less change of flowing over dirt anchoring the dirt inside the paint. A decreased water contact angle leads to a better spread of rain water providing a better cleaning of dirt accumulated at the surface.

Δa change under exposure.

The change of Δa is almost -0,5 for the unmodified paint (green shift) while the paints containing silica have changed slightly less than -0,3.

Δb change under exposure.



The change in delta b under the 9 month exposure period.

The paints with silica had no significant change in colour while the unmodified paint had a shift towards blue in colour. It emphasize the strong dirt pickup of this paint.

Conclusions exterior testing

- The exterior testing confirms the trends detected in the laboratory. We note specifically:
- Higher dirt pick-up resistance with silica
- The 40/220 Bindzil seems to be more effective with all binders than the surface modified more hydrophobic CC40.
- In general the acrylate based paints seem to respond better to the addition of silica