A Waterborne Self Cross Linking Binder for Designing Coatings with Excellent Chemical and Blocking Resistance

Gun Lundsten

CH-Polymers OY, Raisionkaari 55, 21200 Raisio, Finland, e-mail: gun.lundsten@ch-polymers.com

New functionalities for different kinds of surfaces have become an important trend. The current market offers DIY coatings with good chemical resistance and easy-to-clean properties. As a mother of three children and as a busy R&D manager in the chemical industry I have already many years ago realized that by simplifying daily routines in the household you get more time for spending with your family. To fit into my lifestyle the surfaces in my home are therefore painted with easy-to-clean paints. These paints offer good performance, however, I was interested to see if I could improve them still further.

In this paper the properties of a tailor made water borne binder for designing stain resistant and easily cleanable interior paints will therefore be discussed.

Factors Influencing Stain Resistance

One approach to solve the problem with stained surfaces is to completely prevent the stains from interacting with the surface or at least minimize the interaction with the surface. The challenge is therefore to design a paint film resistant to both hydrophilic and hydrophobic stains. One way to achieve this is via a controlled microstructure of the surface, which furthermore has to be based on a non-porous continuous matrix. This stops the stains from penetrating into the film. Earlier studies have shown that resistance to hydrophilic stains is more a function of the binder used in the paint, whereas the resistance to hydrophobic stains is mostly affected by the pigments and fillers in the system. This means that to get resistance to hydrophilic stains the binder should be as hydrophobic as possible.

Figure 1. Stains of red wine can be tricky to remove.

The demand for low VOC and VOC free interior paints brings many challenges in developing a binder with a good blocking resistance and therefore a good stain resistance. Polymer particle morphology is a key tool when designing a binder giving a hard polymer film whilst maintaining a low film formation temperature.

Table I. The Contact Angle of Water to Polymer Films and Paint Films, respectively		STY-BA	MMA-BA	MMA-2-EHA-BA
Contact Angle of Water to Polymer Film	(°)	66	73	79
Contact Angle of Water to Paint Film	(°)	63	71	77

Hydrophobicity of the Binder and Paint

Binders with different monomer composition were prepared. The used monomers were styrene (STY), butyl acrylate (BA), methyl methacrylate (MMA), and 2-ethyl-hexyl acrylate (2-EHA). All binders had a film formation temperature, MFFT, around 0 °C. All binders were formulated with a phosphate ester as the main emulsifier. Solid content of the binders was 45 %.

Paints with different binders were made according to the formulation in Table II. Binders and paints were applied 150 µm wet on clean glass plates and dried in +50 °C for one hour and in room temperature (+23 °C and 50 % RH) for 24 hours. The contact angles of water on the films were determined by a Fotocomp surface energy instrument at 0,5 seconds after application of the water droplet. The results in Table I are average values of 10 measurements. The styrene acrylic polymer has the lowest contact angle and the acrylate containing 2-ethyl-hexylacrylate the highest. As expected the same trend can be seen in the contact angles on the paint films.

Easy-to-Clean Paint, PVC 28	
Raw Materials:	
Pigment grind:	
Water	**56,3**
Rheology Modifier I (Nonionic Urethane)	**8,5**
Polyacrylic Dispersant	**10,5**
Ammonia 25% (aq)	**0,8**
Nonionic Wetting Agent	**1,9**
In-Can Biocide	**1,9**
Defoamer	**0,6**
Titanium Dioxide	**169,6**
Na-K-alumina silicate, 10 µm	**84,8**
Let down:	
Binder, solids 45 %	**497,8**
Defoamer	**0,3**
Rheology Modifier I (Nonionic Urethane)	**6,8**
Rheology Modifier II (Nonionic Urethane)	**7,1**
Water	**153,2**
Total	**1000,0**
Paint Properties:	
Solid Content weight-%	**49,3**
PVC %	**28,3**

Table II. The tested paints were formulated according to the formulation to the left.

Hydrophobicity of Films versus Stain Resistance and Stain Removal

Draw downs (150 µm wet) of the paints were made onto plastic scrub test panels and dried at room temperature for three days. As mentioned above usually binder type and monomer composition have a greater impact on hydrophilic staining than on hydrophobic staining. Therefore hydrophilic stains were tested. The stains included are not a part of any international norm. They were red wine, coffee, black tea, beetroot, mustard, ketchup and nicotine. A 15 mm wide stripe of each stain was applied across the paint film. After a 60 minutes exposure period the excess liquid was absorbed into a soft paper towel and the test panels were immediately placed into a standard scrub machine.

Figure 2. Paint films exposed to water soluble stains for 1 hour and then immediately subjected to 100 scrub cycles. A paint based on the styrene acrylic binder is shown to the left and a paint based on the acrylic binder containing 2-ethyl hexyl acrylate to the right. A problem with the styrene acrylic based paint was that the stains were floating out and connected.

The abrasive pad was replaced by a piece of expanded polystyrene coated with eight layers of cheese cloth immersed into a 5 % aqueous solution of sodium dodecyl benzene sulfonate. The paint films were then subjected to 100 scrub cycles. The test panels were removed from the abrasion tester, rinsed with clean water and dried at room temperature, Figure 2. CIELab measurements were performed on the areas exposed to stains. The difference in color was measured as ΔE between unexposed areas and exposed scrubbed ones. This means that the smaller the ΔE value the better the chemical resistance and the better the stain removal of the paint. The results of the ΔE values of the different stains are shown in Figure 3.

The most difficult stains are the ones of red wine, coffee and nicotine. Generally it can be seen that the main drivers in achieving a good stain resistance is the monomer composition and the hydrophobicity of the film, Table III. This means that the higher the water contact angle the better the stain resistance and the stain removal. Therefore it was decided that further optimization of the polymer composition should be made to increase the hydrophobicity of the polymer film.

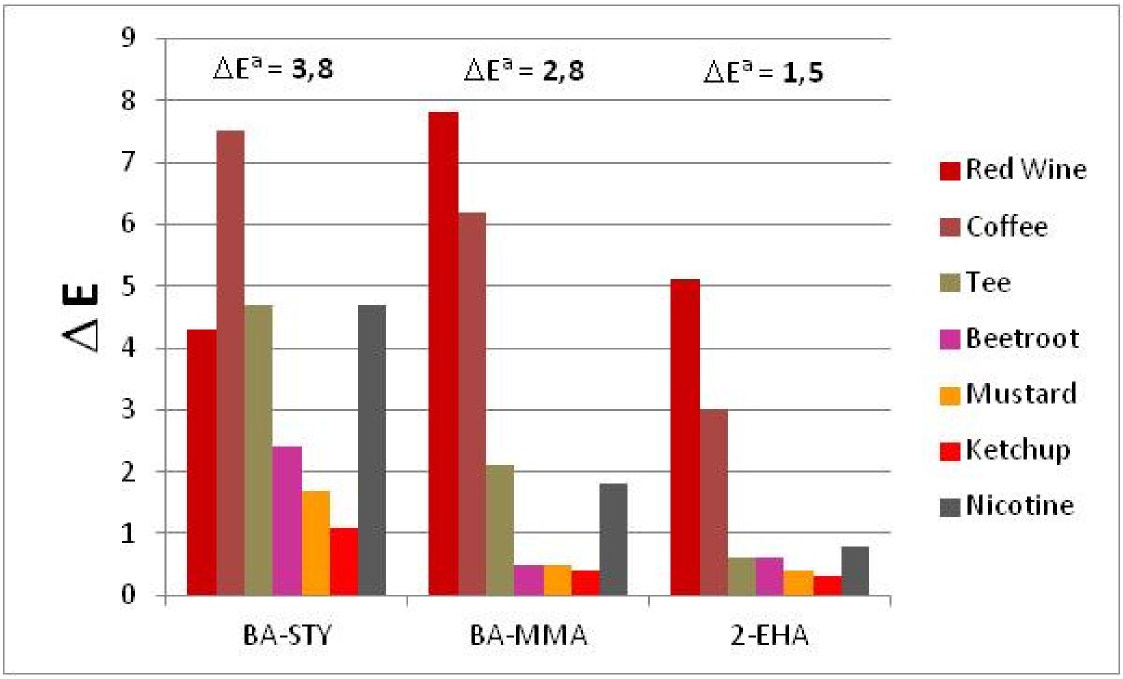

Figure 3. Comparison of different polymer binders in a PVC 28 paint with ΔE indicating the stain removal performance for different house hold stains. ΔE^a is the average ΔE value of the water soluble stains.

Table III. The water Contact Angle to Polymer Films and Paint Films, respectively, compared to the average ΔE for different house hold stains

		STY-BA	**MMA-BA**	**MMA-2-EHA-BA**
Water Contact Angle to Polymer Film	(°)	66	73	79
Water Contact Angle to Paint Film	(°)	63	71	77
Average ΔE of water soluble stains		**3,8**	**2,8**	**1,5**

Optimization of the Polymer Composition

The use of binders with higher glass transition temperature, Tg, gives paints with less dirt-pick-up and stain resistance and furthermore paints with better block resistance. As the application in this case is an interior paint the use of solvents for improving film formation is not desirable. Thus the target was to keep the film formation temperature of the binder close to 0 °C but to achieve a good enough blocking resistance. A traditional way to solve the problem is to take advantage of a core and shell technology, Figure 4. A morphology of the particles with a soft core and a hard shell gives already an improvement of the blocking resistance compared to a homogenous particle. Even higher blocking resistance is usually achieved by a hard core and a soft shell. For further improving the chemical resistance of the soft polymer a cross-linking chemistry could be included.

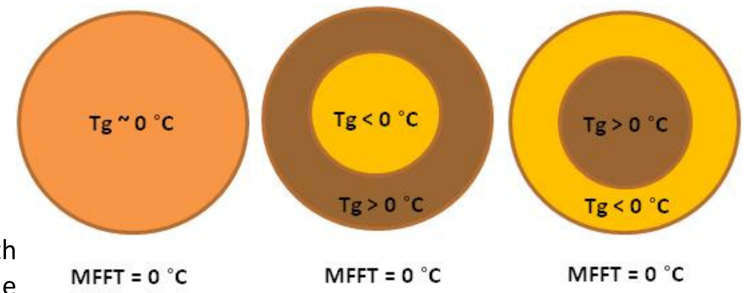

Figure 4. A core-and-shell morphology with a hard core and a soft shell gives usually the best blocking resistance

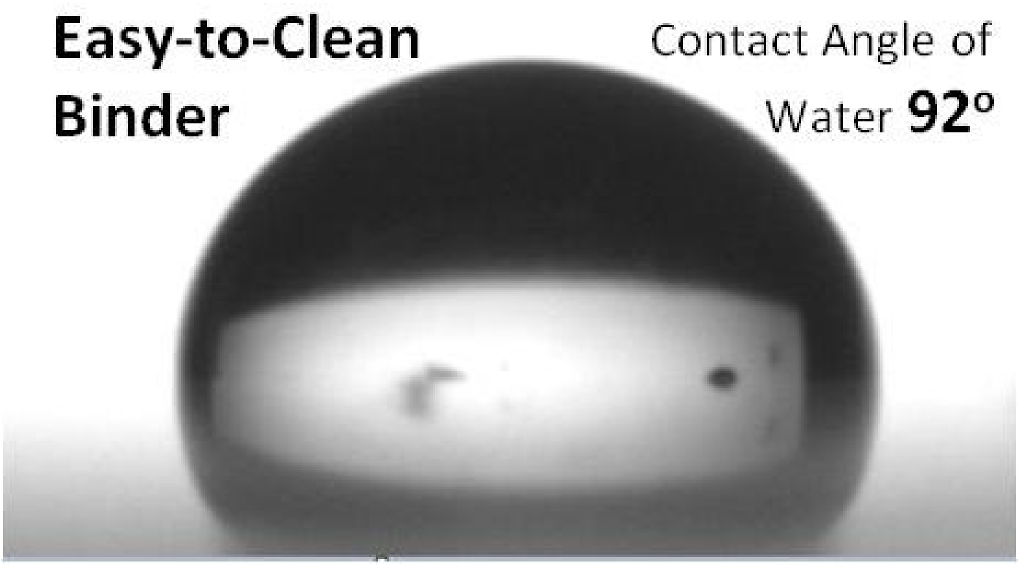

Figure 5. The contact angle of water on the polymer film of the easy-to-clean binder is 92°.

After a long optimization process the outcome is an easy-to-clean binder with good chemical resistance to hydrophilic stains, good stain removal properties and a sufficient blocking resistance. The contact angle of water to the polymer film is 92°, Figure 5, and to the paint film 84°. All tested water soluble stains are more easy to remove and especially red wine, coffee and nicotine. This means that the resulting average ΔE is as low as 0,8, see Figure 6, This average ΔE is well below 1,0, which has been seen as a threshold value for a paint with good performance.

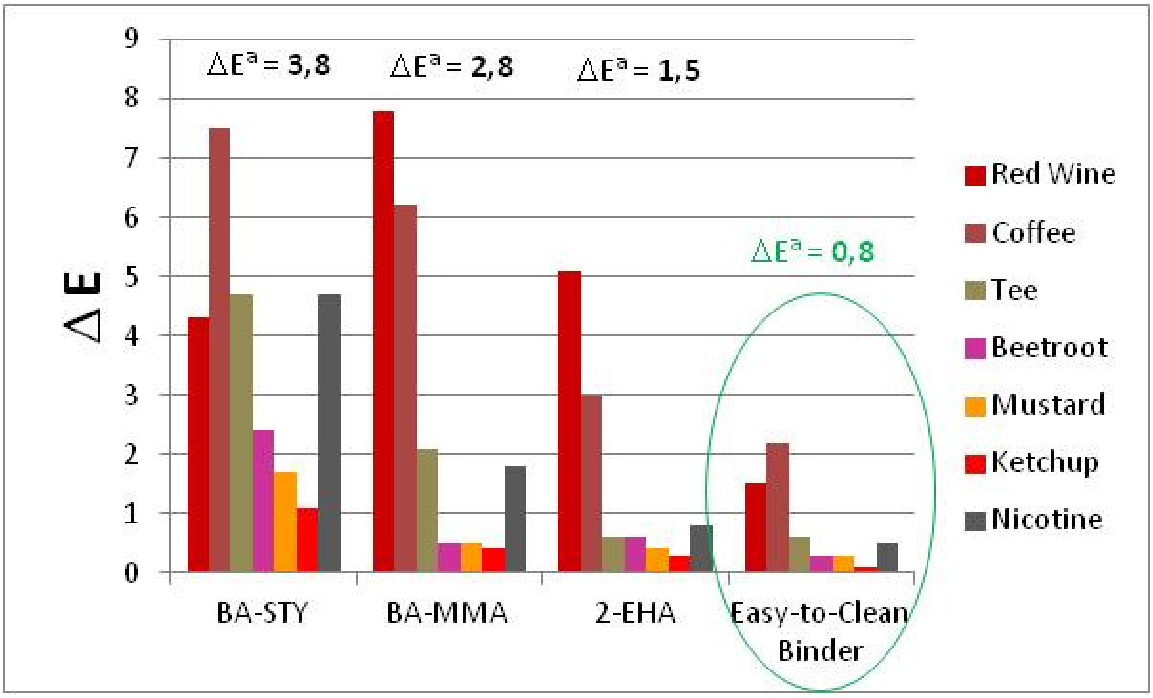

Figure 6. The average of ΔE and especially the ΔE of red wine and coffee are much lower for the paint based on the easy-to-clean binder compared to the paints based on traditional binders.

The blocking resistance of the easy-to-clean paint was determined at +23 °C after three days drying with an ISO 4622 device (0,1 MPa) and was rated 9 (0 = worse, 10 = best), which means that it is sufficient. The scrub resistance of the paint film was determined according to ISO 11998 and classified to class 1 according to EN 13300. The adhesion to old glossy alkyd is excellent.

Effect of Pigment Volume Concentration on the Stain Removal

To investigate the effect of the pigment volume concentration, PVC, on the chemical resistance and stain removal properties paints based on the easy-clean binder with PVC 18 and PVC 40 were prepared and tested in the same way as earlier. The results are presented in Figure 7.

A lower PVC than 28 does not considerably improve the stain resistance nor the stain removal properties. The average ΔE is on the same level for both PVC 18 and PVC 28. At PVC 40 a decrease in the easy-clean properties can be seen. A higher PVC increases the porosity of the surface and leads to a deeper penetration of the stains into the surface.

In the near future the effect of different PVCs and different fillers will be investigated in more detail. As the stain resistance and stain removal of hydrophobic stains are dependent on the types of pigments and filler used the stain removal of hydrophobic stains will be tested at the same time.

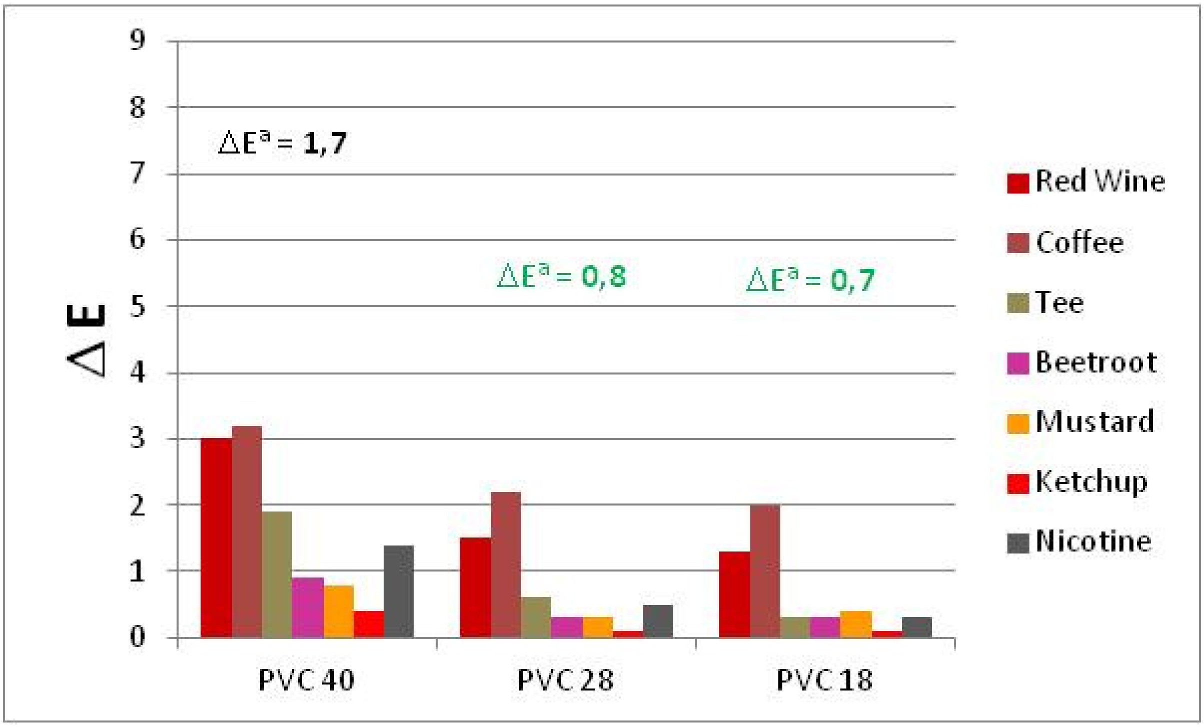

Figure 7. The average ΔE at different PVC of paints based on the easy-to-clean binder. The gloss at 60° for the PVC 40 paint is 15, for the PVC 28 paint 24 and for the PVC 18 paint 80. The effect of PVC on the stain removal properties will be investigated in more detail in the near future.

Summary

By increasing the hydrophobicity of the polymer a binder with excellent resistance to hydrophilic stains can be produced. By further optimizing the morphology of the polymer particles a combination of good film formation at 0 °C and good blocking resistance at ambient temperatures can be achieved.

As the next step the effect of the formulation and especially the effect of pigments and fillers will be investigated. As these are the key factors contributing to hydrophobic stain removal properties, a more detailed study of these features will be made.

Acknowledgement

Application Specialist **Saija Vehviläinen** is thanked for the comprehensive laboratory work including synthesis of the binders, preparation of the paints and execution of the tests. Other colleagues are thanked for their valuable comments on this paper.

References

Andrew Edward Moody et al: “Oleophobic, hydrophilic coatings: the optimum system for exterior dirt pick up resistance”, European Coatings Conference “Easy-to-Clean / Self Cleaning Coatings” Berlin 29 – 30 November 2007

Inka Henze: “Durable easy-to-clean coating for home application”, European Coatings Conference “Easy-to-Clean / Self Cleaning Coatings” Berlin 29 – 30 November 2007

Jean Meng: “Novel applications in low VOC coatings”, Polymer Paints Colour Journal March (2012) pp. 16-27

Gun Lundsten et al: “A styrene acrylic dispersion for VOC free paints and plaster”, Advances in Coatings Technology, Warsaw, 28-30 November 2006, Paper 7

Oliver Schmidt: “The wetter the better”, European Coatings Journal 04 (2010) pp. 40-44

Oliver Wagner et al: “Raising the barriers to dirt”, European Coatings Journal 10 (2010) pp. 32-37