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CLOSING THE GAP BETWEEN

Water and Solventborne Anticorrosion Coatings via New Binder Concepts

Water-based anticorrosion resins have gone through many stages of evolution. Despite steady progress, there is still need for improvements. Recent innovations in the area of polymer colloids and hybrid materials offer new opportunities to develop novel coatings for metal protection.

By choosing the appropriate technology, it is possible to design acrylic binders with improved barrier properties, low water uptake, and improved anticorrosion properties. Different methodologies will be discussed, including: designed particle morphology, engineering of the water phase composition, and the use of hybrid binders. Also, a new technology exceeding basic barrier function will be presented. This utilizes a built-in, enhanced corrosion protection mechanism resulting in outstanding performance in salt-spray and early rain resistance.

INTRODUCTION

The more stringent environmental standards and new technology advances are pushing forward waterborne coatings for corrosion protection. Currently, most of the research and development effort is focused on reducing the volatile organic content (VOC) content in architectural and industrial coatings. Because the film formation in polymer dispersions is greatly assisted by the use of organic solvents, the pursuit of low-VOC formulations can be detrimental to film formation and, consequently, result in poor barrier properties. As a result of the substantial effort in the field, many new waterborne paint technologies have been launched (high performance acrylics, epoxy esters, alkyds, zinc-rich epoxies, fluoropolymers, polysiloxanes, etc.).[1-3] Despite the fact that waterborne systems still hold a relatively low share of the total market for anticorrosive coatings, the average growth rate for waterborne coating technology is larger than that for conventional solventborne coatings. Other benefits of waterborne coatings are the reduction of worker exposure to organic solvents and of fire hazards in confined areas.

Water-based acrylic anticorrosion resins are not new in the market, and they have gone through different developments in the last 20 years with the aim of replacing solvent-based systems. The first waterborne systems appeared in the market in the 1960s and were based on formulations containing simple acrylic copolymers with red lead or zinc chromate. Further developments led to lead- and chromate-free systems. The next generation systems, well established and state-of-the-art, combine more sophisticated modified acrylics with modified zinc phosphates and borates. Nevertheless, there is still enough space for further improvements of aqueous anticorrosion paints, e.g., in barrier properties, increasing their potential and, in turn, widening their application spectrum. Thus, it should be possible to reach the last required properties to equal the performance of traditional solventborne systems offering the opportunity for substitution.

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WATER-BASED ACRYLIC DISPERSIONS: HIGH PERFORMANCE AND ENVIRONMENTALLY FRIENDLY

Waterborne acrylic dispersions are mainly used in mid- and light-duty coatings for the maintenance (bridges, plant and industrial equipment, repainting, towers, etc.), transportation (trucks, buses, trains, tractors, mining trucks, etc.) and do–it-yourself (DIY) (repair, general maintenance, steel building panels, etc.) segments among others. Very often these coatings are applied as multicoat systems that include several layers:

- *Primers*, having the function of providing good corrosion protection and adhesion to the metal surface
- *Intermediate coats*, acting as a barrier to moisture and aggressive chemicals and help to build film thickness
- *Topcoats*, responsible for the aesthetics, but also for better impermeability and weatherability

Alternatively a monocoat may be applied, the so-called direct-to-metal (DTM) coatings, with minimal surface preparation. DTM coatings are attractive due to the reduction of application steps (no surface preparation and only one applied coating), the reduction of raw material costs (one coat versus many), and the lack of the necessity of using active pigments. DTM coatings, however, do not often display the superior properties of a multicoat system and are typically used in lighter duty applications.

Waterborne acrylic dispersions are suitable for all of the above-mentioned applications. The main advantages and limitations of waterborne acrylic dispersions for anticorrosive coatings are summarized in *Table* 1.

Table 1—Main Advantages and Limitations of Waterborne Acrylic Binders for Anticorrosive Coatings

Advantages

- Health, safety, and environment (HSE), due to very low organic solvent content
- Fast drying and recoating times
- Low odor
- Good corrosion protection
- Water as main solvent (also used for cleaning and thinning)
- Low flammability
- Good hardness development and chemical resistance
- Low dirt pick-up (topcoats)
- High degree of flexibility
- Competitive in price
- Suitable for forced drying

Limitations

- Not appropriate for underwater use
- Complex film formation process
- Limitations regarding climate conditions at application (high RH[a] and low T)
- Require excellent surface preparation
- Foaming problems
- Corrosion/flash rust (solved by addition of a corrosion inhibitor)

(a) RH: relative humidity.

A typical anticorrosion paint formulation is composed of four main components: a binder, one or several co-solvents, barrier and active pigments/fillers, and additives. The binder constitutes the backbone of the coating system (comprising about 40% of the total formula) and helps to bind the pigment particles together and achieve a good adhesion of the coating to the metal surface. Generally, styrene-acrylic binders are preferred because they provide better water and alkali resistance than straight acrylics. Typically self-crosslinking binders are used with a glass transition temperature (T_g) above 20°C. To achieve good film formation and complete coalescence of polymer particles at the application temperature (typically < 60°C), co-solvents (glycol ethers, glycol ether acetals, alcohols, etc.) are added in small amounts. They are employed to reduce the minimum film forming temperature (MFFT) of the binder, typically in a mixture of hydrophilic (e.g., butyl glycol) and hydrophobic (e.g., dipropylene glycol n-butyl ether) solvents. The push from the market to further reduce the VOC content (by reducing the organic solvent content) and obtain environmentally friendlier paint formulations can have a negative influence on the film quality, resulting in a poor particle coalescense, poor barrier properties, and therefore, an early failure of the coatings. To further reduce the VOC content in waterborne paints, it is necessary to move from standard styrene-acrylics towards more sophisticated polymer architectures that allow optimal film formation under low VOC conditions.

The pigment volume concentration (PVC) of anticorrosion coatings is in the medium range somewhat below the critical PVC with typical values of approx. 30%; the only exceptions to this rule are direct-to-metal (DTM) high-gloss lacquers which are lower in PVC as well as zinc-rich primers which are higher in PVC and may even exceed the critical PVC. Thus, the amount of binder more or less equals the mass of pigments and fillers leading to

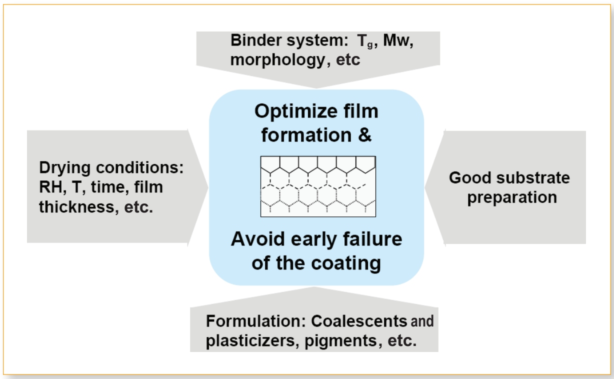


Figure 1—Key factors that must be considered to optimize film formation of anticorrosion paints and avoid early failure of the coating.

the direct consequence that both components have significant influence on anticorrosion performance. The formulation typically contains different types of pigments and fillers. Pigments such as titanium dioxide or red iron oxide provide aesthetic properties (such as color and opacity) and decrease the permeability of the film. Extender pigments such as calcium carbonate, mica, talc, and clay reduce cost and enhance certain properties by building up a resistant barrier to corrosive substances (water, ions, oxygen). Active pigments such as zinc phosphates provide additional corrosion protection to the coating. The pigment-binder interaction is critical to obtain an effective barrier and binders are typically designed to obtain an optimal pigment distribution within the coating formulation. Large pigment agglomerates that can lead to defects in the coating must be avoided to assure an optimal anticorrosion performance. Improving the pigment-binder interactions enhances the barrier properties of the coating and effectively increases the volume occupied by the pigment/filler.

Several additives that facilitate the manufacturing, application, and performance of the coatings are also included in the formulation. These additives are present in smaller amounts and include surfactants, plasticizers, thickeners, flash rust inhibitors, and pigment dispersing agents, among others.

KEY FACTORS AFFECTING FILM FORMATION, BARRIER PROPERTIES, AND ANTICORROSION PERFORMANCE

To avoid early failure of the coating and ensure good corrosion protection, the use of a well-performing binder is a must—but it is not the only factor playing a key role. In addition, to achieve an optimal film formation and thus avoid an early failure of the coating, good substrate preparation, the development of an appropriate formulation, and the drying conditions are as important as selecting an appropriate binder system for the coating (see *Figure* 1). Ideally, oils, corrosion, and any other contaminants must be eliminated from the metal substrate prior to applying the paint. This is of paramount importance, since in many cases early failure of coatings is due to either inadequate surface preparation or improper application of the coating to the substrate. In the special case of DTM coatings, there may be little or no surface preparation before coating. Often times, such coatings are applied over oily substrates without previous cleaning or other type of substrate preparation. Proper formulation will enable the manufacture of paints that overcome this challenge.

As mentioned in *Table* 1, one of the limitations of waterborne acrylics for this application is that film formation and thus coating quality is quite susceptible to climatic factors, especially at low temperatures (Ts) and high relative humidity. Thus, it is important to take into account the drying conditions under which the paint is applied and to keep in mind that they can under extreme T and RH conditions lead to poor film formation, despite the use of an excellent binder and formulation (see

Figure 2—Poor film forming of an anticorrosion paint under low application temperatures (<5°C) and/or low coalescent amounts.

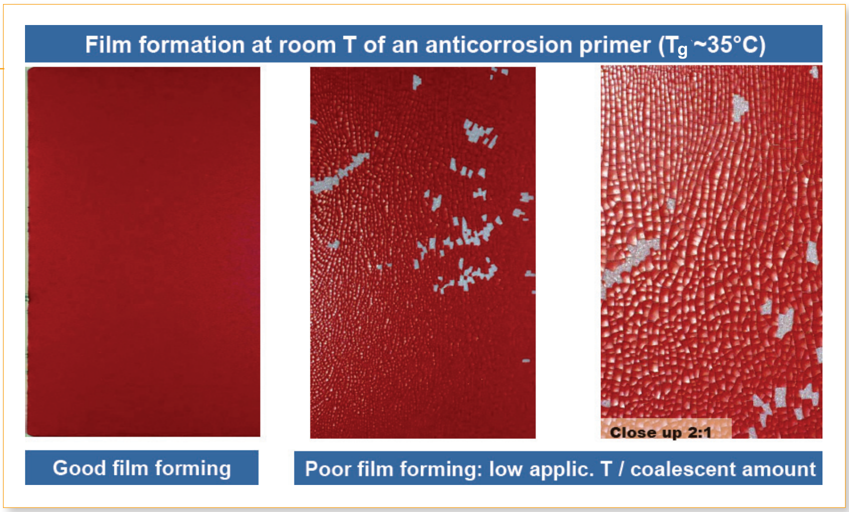


Figure 2). *Figure* 3 shows the effect of the RH on the early water-spot resistance of a commercial styrene-acrylic binder. The application of the same coating (based on a styrene-acrylic dispersion) under high RH conditions resulted in strong blistering, poor early water-spot resistance, and early failure of the coating. Therefore, understanding the influence of T, RH, and ventilation requirements helps to avoid early failure of the coating system.

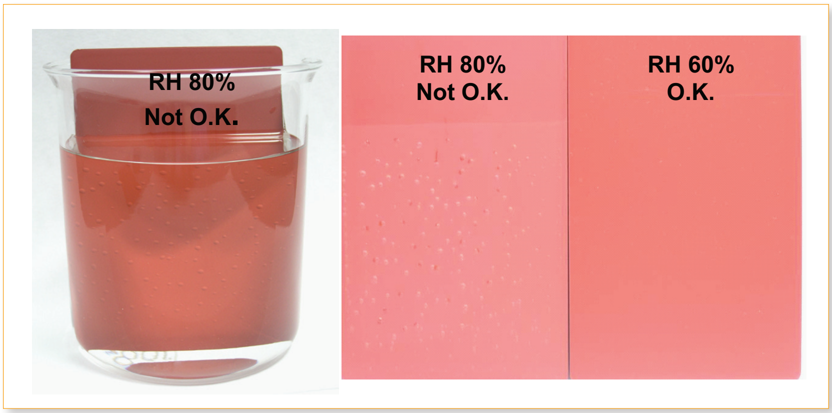


Figure 3—Effect of RH on the early water-spot resistance of commercial anticorrosive paints. Application of the waterbased coating under high RH conditions can lead to strong blistering and early failure of the coating.

NEW APPROACHES TO HIGH-PERFORMANCE WATERBORNE ACRYLIC DISPERSIONS

The degradation of coated metal parts takes place when water and oxygen penetrate the coating film, causing the separation of the paint from the metal.[4] When water and ions reach the polymer-metal interface, electrochemical reactions will take place that lead to the appearance of rust. This process starts in defects such as scratches, pores, or regions of the paint with reduced crosslinking density. Therefore, a coherent and defect-free polymer film is the basic requirement for an effective protection of the metallic substrate, because interstices and film defects (as shown in *Figure* 4) act as pathways for water and ion diffusion that accelerate the corrosion of the metal surface.

One way to avoid—or at the minimum, delay—the corrosion process is the development of binders with improved barrier properties and adhesion to the metal surface. Approaches to achieve good adhesion between coating and metal are the incorporation of functional groups into the binder and decreasing the permeability of the polymeric film. This will prevent water and ions from penetrating through the coating and reaching the metal substrate. The barrier properties can be improved by designing binders with improved film-forming properties (e.g., lower MFFT by maintaining a high T_g/blocking resistance) or with reduced water uptake (e.g., via engineering the water phase or using hybrid materials with very low water uptake).

Recent innovations in the area of polymer colloids and hybrid materials offer new opportunities to develop novel coating formulations for anticorrosion applications. BASF has followed several approaches and developed a new generation of water-based anticorrosion resins with improved performance. The different approaches will be described in the following sections and are based on designed particle morphologies, engineering the water phase and the use of hybrid materials. Several binders were developed using these concepts. Based on the existing work involving structured particles, a binder was developed that has two roles: it acts as a barrier and as a corrosion inhibitor. The function of this new binder is beyond mere binding of the polymer particles and goes one step further by actively preventing/delaying corrosion. Furthermore, two key parameters were explored to develop a second binder: minimization of water soluble materials in the continuous phase and optimization of film formation in order to maximize barrier properties. Finally, two different hybrid binders were developed. These binders resulted in coatings with improved barrier properties and extremely low water uptake. By combining two different materials during the binder synthesis, new hybrid products with improved anticorrosion performance were obtained.

Waterborne acrylic dispersions are commonly prepared via emulsion polymerization, which presents several advantages in comparison to solution polymerization. One advantage is the synthesis of polymers with much higher molecular weights.

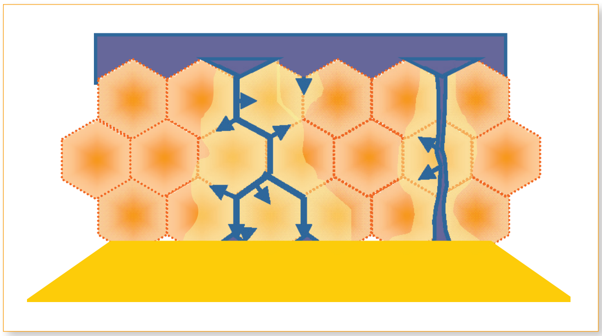


Figure 4—Interstices and film defects act as pathways for water and ion diffusion accelerating the corrosion at the metal-coating interface.

Table 2—Primer Formulations Used to Prepare the Anticorrosion Primer Coatings Tested

	Component	Form. 1[a] (wt%)	Form. 2[a] (wt%)	Form. 3[b] (wt%)
Binder	(50% solids, pH=8,5: Formulation 1 and 2) (45% solids, pH = 8: Formulation 3)	43.4	46.7	59.5
Pigments	Active pigment: zinc phosphate Red oxide Fillers: talc, $BaSO_4$, ZnS (Formulation 3 does not contain active pigments or fillers, only TiO_2)	45.8	29.8	16.6
Co-solvents[c]	BG, MS (180-210°C), PPh (Formulation 1, 2) EB, DB, PG, Tex (Formulation 3)	2.3	2.6	8.5
Additives	PU thickener Corrosion inhibitor Pigment dispersant Flash rust inhibitor (Formulation 3 has no corrosion inhibitor, except flash rust inhibitor)	1	3	3.8
Water		7.5	17.9	11.6
Pigment Volume Concentration (PVC, %)		34	25	13
Solids content (%, weight)		66	61	45.6
VOC (g/l)		80	80	240
pH		>9.5	>9.5	>8.5

(a) In formulation 1 and 2, the pH of the paint was adjusted to 9.5 using ammonia.
(b) In formulation 3, no pH adjustments were made.
(c) BG: butyl glycol; MS: mineral spirit; PPh: propylene glycol phenyl ether; EB: ethylene glycol n-butyl ether; DB: diethylene glycol n-butyl ether; PG: propylene glycol, Tex: Texanol®.

This reduces the need of post-curing the coating to obtain appropriate mechanical properties. Another advantage is that the resin is obtained in the form of a dispersion of high solids content (50% or higher) and low viscosity, thus allowing fast air drying by evaporation of water. When developing dispersions for any application, one has to consider that emulsion polymers are "products-by-process" whose main properties are determined during the polymerization process. Therefore, a deep understanding of how to use the polymer microstructure (molecular weight distribution, polymer composition, branching and crosslinking density, particle morphology, and particle size distribution) in order to affect the anticorrosive properties, is necessary. By designing the polymer architecture of the latex particles in a way that leads to better film forming, pigment distribution in the paint formulation, and high barrier properties, the anticorrosive performance of the existing styrene-acrylic binders can be enhanced, thus closing the performance gap versus their solventborne counterparts.

Despite the many advantages of the emulsion polymerization process, some negative features are contrary to the goal of superior corrosion resistance. For example, the use of surfactants to stabilize the emulsion can lead to water susceptibility. Careful selection of these stabilizers can minimize this effect. Also, polymerization does not happen exclusively in the latex particles. Polymerization can also occur in the water phase when water-soluble monomers are present. This leads to hydrophilic oligomers and, therefore, increased water permeability of the resultant film. The resulting binder is a combination of polymer particles and a water phase that is highly influenced by the polymerization parameters. Unfortunately, all the mentioned water-soluble species can negatively influence the water sensitivity of the coatings and promote corrosion. Careful engineering of the polymer system, however, can minimize these potential concerns. Proper choice of surfactants, monomers, and polymerization conditions can provide polymer dispersions with superior corrosion resistance.

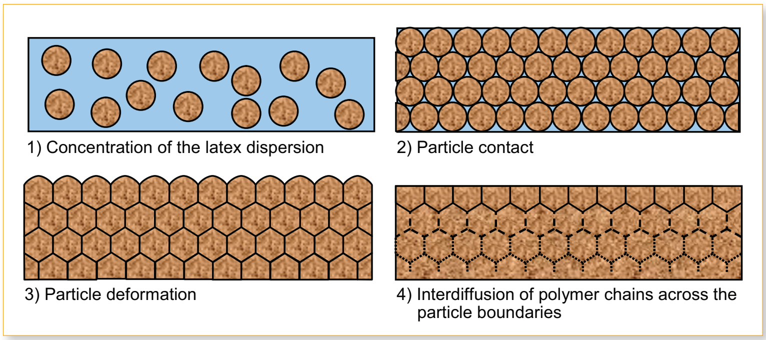


Figure 5—Schematic representation of the different stages during the film-forming process.

Designed Particle Morphology for Improved Anticorrosion Performance

The particle morphology of a latex is a very important property, since it is directly related to the film morphology and quality. This has a direct effect on the anticorrosion performance of coatings. There are plenty of publications in the open literature where different strategies to achieve different particle morphologies (core-shell, inverse core-shell, raspberry, snow-man, etc.) are discussed. Among all the works, the majority of them are devoted to the production of core-shell particles, usually achieved by employing a two-stage polymerization process. Typically the core is produced during the first feed, and in the second one the monomer(s) forming the shell are added into the reactor.[5-8]

The film-forming process of a latex is a complex mechanism that includes four different stages, schematically shown in *Figure* 5. These stages are: (1) the concentration of the latex dispersion; (2) particle contact; (3) particle deformation; and (4) the inter-diffusion of the polymer chains across the particle boundaries, which is necessary to form a mechanically stable film.[9-10] The end-use properties of the latex (mechanical and optical properties to mention a few) are strongly influenced by the film formation process. Typically, only the outer shell of the polymer particles takes part in the fourth stage, namely the interdiffusion of the polymer chains into the neighboring particles. Therefore, this outer layer is largely responsible for proper film formation. This last stage of the film-forming process is of paramount importance to obtain coatings with good early water-spot resistance.

Although this film formation is facilitated by lower molecular weight and lower T_g polymers, a certain hardness of the polymer film is necessary to assure good barrier properties and durability. Unfortunately, an increase in hardness either via higher content of hard monomers (such as styrene) or crosslinking (using functional monomers) usually has a negative influence on the film formation, in particular on the inter-diffusion of polymer chains across the particle boundaries. This leads to poor early water-spot resistance and to early failure of the coatings under corrosive environments.[11] Also, a fundamental understanding of the film formation process can greatly benefit chemists seeking to optimize this feature at a given VOC. Taylor, et al.[12] have performed such theoretical studies. These model studies predict the extent of film formation in a given latex, as well as property development in a variety of solvents.

One way to overcome this problem and obtain coatings with good hardness and good barrier properties, while maintaining good elasticity and early water-spot resistance, is the use of structured polymer particles. Core-shell polymers, composed of a core that provides good hardness and durability with a soft shell that exhibits good elasticity and coalescing properties,[3] result in coatings with better anticorrosive properties. The harder core reduces significantly the diffusion constants of water and thus, ion permeation, slowing down the corrosion of metal surfaces considerably.

To prove the effect of particle morphology on the quality of the resulting polymer films and on the anticorrosive behavior of the coatings, two dispersions of similar T_g (approx. 32°C) were synthesized (solids content = 50%). Latex 1 had homogeneous particle morphology, being the copolymer composition constant in the whole polymer particle. Latex 2 was synthesized via multistage emulsion polymerization, resulting in core-shell particles, where the shell was softer in order to enhance film formation and avoid defects and interstices that would accelerate water and ion diffusion. Both dispersions were formulated in the same way, following the Formulation 1 in *Table* 2 and coated onto cold-rolled-steel (CSR), resulting in a dry film thickness (DFT) of approx. 80 µm. As it can be seen in *Figure* 6, the coating based

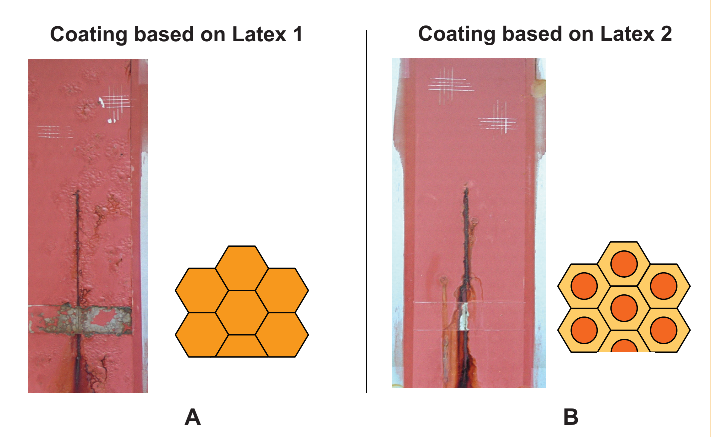


Figure 6—CSR panels after 400 hr of SST. A: coating prepared with Latex 1. B: coating prepared with Latex 2.

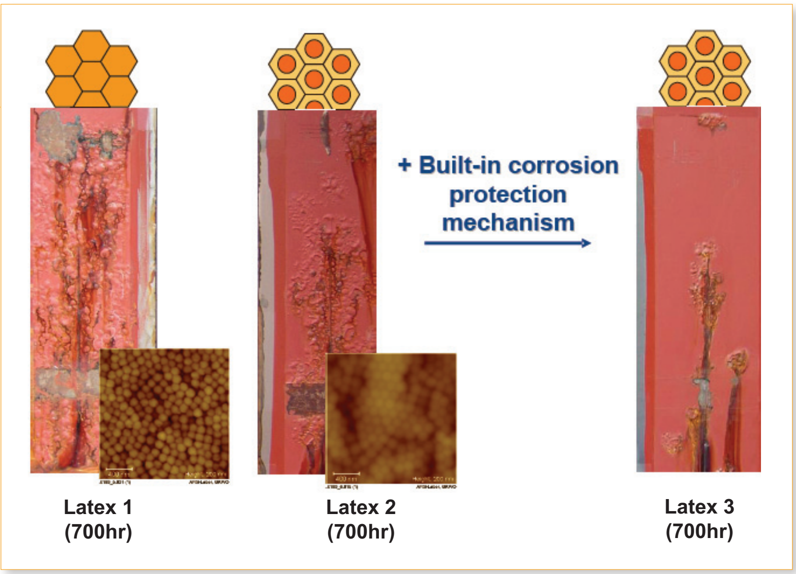


Figure 7—Performance of Latexes 1, 2, and 3 after 700 hr SST. Substrate: CRS. DFT: ca. 80 µm. The AFM figures confirm the improved film forming of the dispersion at room temperature (note that the AFM measurements were done using the pure binders without any additives and organic solvents).

on Latex 2 shows superior performance after 400 hr of salt spray test (SST) in comparison to Latex 1.

BARRIER AND INHIBITING WATERBORNE DISPERSIONS

Utilizing the previously described know-how on structured styrene-acrylic dispersions, a new technology was developed to design a binder having two roles, namely, it acts as a barrier and as a corrosion inhibitor. This was achieved via a built-in enhanced corrosion protection mechanism that results in improved salt-spray test and good early water-spot resistance. The concept behind this approach is to combine the previously described core-shell technology with functional groups that act as corrosion inhibitors (such as phosphate, hydroxy, carboxy, amine, and epoxy groups among others). Important parameters to achieve optimal anticorrosive properties are the type and amount of functional groups incorporated into the binder and their distribution between the surface of the polymer particles and the water phase. As it is well known, the incorporation of certain functionalities, such as the ones mentioned above, can as well improve adhesion to the metal substrate and enhance pigment distribution, thus, improving resistance to corrosion.

Table 3—Overview of the Different Binders Used in This Study

Binder	Description	Technical Approach	SC (%)	pH	MFFT (°C)
Latex 1	Sytrene-acrylic dispersion	Standard Emulsion Polymerization (EP)	50	8.5	22
Latex 2	Sytrene-acrylic dispersion (core-shell)	Designed particle morphology	50	8.5	22
Latex 3	Modified sytrene-acrylic dispersion (core-shell)	Designed particle morphology + built-in corrosion protection mechanism	50	8.5	22
Latex 4	Styrene-acrylic	Engineering the water phase	45	8	26
Latex 5[a]	Dispersion comprising a hydrophobic polymer	Emulsion polymerization	50	8.5	0
Hybrid 1	Acrylate-hydrophobic polymer hybrid dispersion	Hybrid material with improved barrier properties	50	8	20
Hybrid 2	Acrylate-alkyd hybrid dispersion	Hybrid material with improved barrier properties	42	8	1

(a) Latex 5 is an acrylic-free composition.

To check the effect of the incorporation of corrosion-inhibiting functionalities in the binder, a dispersion (Latex 3) based on the recipe of Latex 2 but containing the functional groups under study was synthesized. Latex 3 should therefore show all the advantages of Latex 2 regarding a better balance of film-forming and barrier properties, in addition to a better corrosion inhibition due to the functional groups. Latexes 1, 2, and 3 were formulated following the Formulation 1 in *Table* 2 and coated onto CSR, resulting in a DFT of approx. 80 µm. *Figure* 5 shows the performance of the three coatings after 700 hr of SST. As already shown in *Figure* 6 the performance of Latex 2 is again better than the one of Latex 1, although both coatings show severe failure after 700 hr exposure to SST. The coating based on Latex 3 shows superior performance, due to the built-in corrosion-inhibiting mechanism (see *Figure* 7).

DISPERSIONS DESIGNED FOR DTM VIA SUPERIOR FILM FORMATION AND MINIMIZATION OF WATER-SOLUBLE COMPONENTS

The use of the emulsion polymerization process to produce coatings binders necessitates the presence of surfactants. These surfactants all have a degree of hydrophilic character and this can promote water transmission and the acceleration of corrosion. Also, although it is desired for all polymerization to occur in the emulsion particle, many monomers have a degree of water solubility. This is especially true for those that may be used to help stabilize the polymer particles and/or improve adhesion such as methacrylic and acrylic acid. Since free radicals are present in the water phase as well as in the particles, these monomers may form water-soluble oligomers that can increase the ease of transport through the applied paint film in which the polymer dispersions are used. All effort must be made to minimize the presence of these materials in the water phase.

Elimination of the water-soluble components in the aqueous phase is only one feature in designing a superior barrier coating. One must also provide superior film formation, at the desired application VOC and temperature. By careful design of the polymer composition and choice of solvent package, a chemist may achieve the optimum balance of VOC and film formation properties for excellent corrosion protection. The described principles were used to generate Latex 4 (See *Table* 3).

The choice of solvent (in addition to other formulations parameters) is critical to the performance of anticorrosive DTM coatings. Also, the substrate to which they are being applied has a dramatic impact. In the case of direct-to-metal coatings, anticorrosive pigments are not used. Also, the final dry film thickness is typically low (20-40 µm). The inhibition of the rusting mechanism must take place through the engineering of dispersions and formulations that have superior resistance to the migration of water and ions. This cuts off one necessary element of the corrosion process. Several test latexes were synthesized and solvent packages were optimized based on this theory. The final system, designed for 240 g/L VOC with 100 g/L capability, had excellent salt spray resistance at thin film build (20—40 µm). The 240 g/L paint formulation is shown in Formulation 3, *Table* 2. Salt spray results are shown in *Figure* 8.

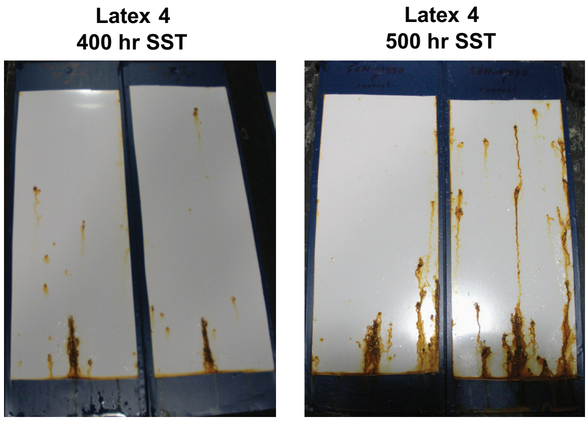
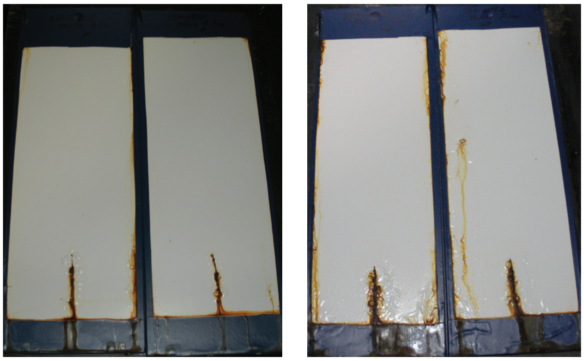


Figure 8—Latex 4 in a 240 g/L white formulation at thin film build.


CRS, clean, polish at 1000 hr SST

CRS, clean, unpolished at 800 hr SST

Figure 9—Latex 4 in a 240 g/L formulation at thick film build over polished and unpolished cold rolled steel.

Barrier properties improve dramatically at thicker film build. This is due to the fact that thicker films increase the time required for diffusion of mobile, corrosion promoting molecules to reach the metal surface. Because this migration is delayed, corrosion is resisted for a longer period of time. Formula 3 (see *Table* 2) was also used to spray thick films (DTF = 80 µm). These materials displayed excellent corrosion inhibition due to the effect of thicker films and their excellent barrier properties (see *Figure* 9).

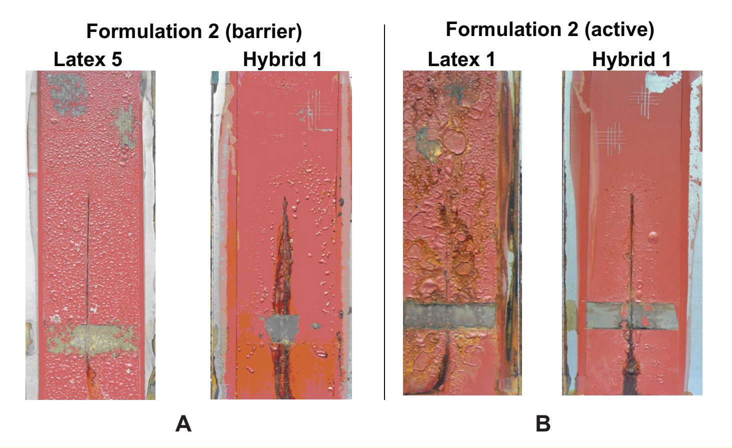


Figure 10—A: performance of Hybrid 1 in comparison to the hydrophobic polymer in the barrier formulation after 350 hr SST. B: performance of Hybrid 1 in comparison to Latex 1 in the active formulation after 720 hr SST (Substrate: CRS. DFT: 80 µm).

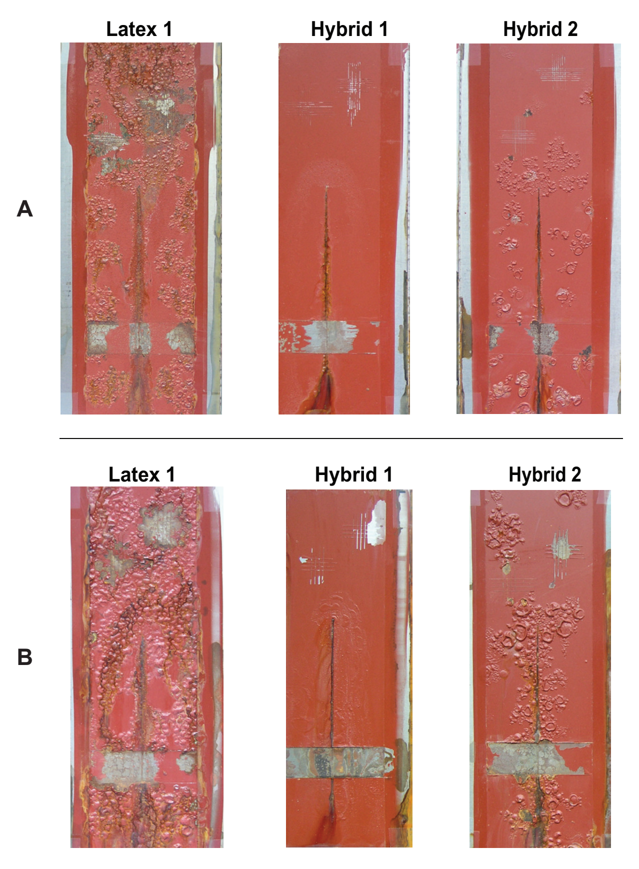


Figure 11—Performance of Latexes 1 and Hybrids 1 and 2.
A: performance after 200 hr SST. Substrate: CRS. DFT: ca. 45 µm.
B: performance after 530 hr SST. Substrate: CRS. DFT: ca. 80 µm.

NOVEL HYBRID DISPERSIONS FOR ANTICORROSIVE PRIMERS

During the last decade, many patents and publications devoted to composite and hybrid materials have been published. The objective of these works is to combine existing materials to form new hybrid products that are superior to the ones with the original components alone. Hybrid materials can be obtained either by simple blending of two (or more) components, or by hybridization during the synthesis step. As often reported in the literature, blending can lead to incompatibility problems and phase separation of the different materials. Therefore, films made of such blends have often macrodomains of each component and in many cases no improvement in the target property(ies) is (are) achieved. A more promising way to obtain hybrid materials with improved performance and have a combination of the different components at nanoscale level is to perform the hybridization during the material synthesis. The main challenges in this approach with emulsion polymerization as the synthetic method are the sometimes poor compatibility of different polymers (i.e., acrylates and alkyds) and the impact on the polymerization process (e.g., retardation, large residual monomer amount).

In this section two newly developed hybrid binders that provide improved anticorrosion properties in comparison to the state-of-the-art sytrene-acrylic binders will be presented. In both cases, the objective was to produce new materials, keeping all the advantages of acrylic binders (flexibility, adhesion, and good film formation among others) in addition to new properties coming from the second component. In the first example (Hybrid 1), the second component used was a very hydrophobic polymer, with very low water uptake and high barrier properties. In the second example (Hybrid 2), the second component used was an alkyd resin with superior chemical resistance and barrier properties versus standard acrylates. For the sake of brevity, details on the synthesis of both hybrids will not be covered in this publication. In *Table* 3 an overview of the different binders used is given. The binders Latex 1 and Latex 5 were used for comparison purposes. All of the binders were formulated using the Formulation 2, shown in *Table* 2. In addition, in the case of Hybrid 1 and Latex 5, a variation in Formulation 2 was used by replacing the active pigment with calcium carbonate. This variation was called Formulation 2 (barrier) in order to differentiate it from the Formulation 2 (active) shown in *Table* 2.

During the development of Hybrid 1, the first attempts to obtain anticorrosion coatings were made using a dispersion composed only of the hydrophobic polymer (Latex 5). This caused large stability problems in the formulation, and poor performance in the SST (failure after 100 hr). This was improved by optimization of the formulation, but still the performance was far from satisfactory (see *Figure* 10A). The most significant improvement in performance was only achieved when the hydrophobic polymer was combined with an acrylic polymer. This resulted in better film quality and, therefore, in a superior corrosion protection. *Figure* 10A shows that Hybrid 1 outperforms the other dispersions, even in the barrier formulation,which contains no active pigment. From *Figure* 10B it can also be seen that after 720 hr of SST the performance of the coating based on Hybrid 1 is much better than the one of Latex 1 (standard styrene-acrylic dispersion).

Further comparisons were carried out between both hybrids and Latex 1; this time at two different DFT. As depicted in *Figure* 11A, Latex 1 showed complete failure after 200 hr SST at low DFT (45 µm), although one must point out that many other systems also present problems with such thin coatings. Hybrids 1 and 2 showed excellent performance due to the improved barrier properties and low water uptake; both features are a result of the hybridization. As shown in *Figure* 11B, the performance of both hybrids was superior to the one of Latex 1 after 520 hr SST, for coatings with a DFT of 80 µm.

CONCLUSIONS

Despite the fact that waterborne systems hold a relatively low share of the total market for anticorrosive coatings, their average growth rate is greater than conventional solventborne coatings. The large R&D effort in the field of waterborne anticorrosion resins has resulted in binders showing excellent performance when applied under suitable conditions (i.e., proper substrate preparation, appropriate T, and RH). The results presented in this work confirm the high potential of waterborne acrylic binders to replace established solventborne systems.

As shown in the first part of this work, the use of structured core-shell particles resulted in better film quality and increased anticorrosion performance. This example illustrates how by designing the polymer architecture of the latex particles in a way that assures better film forming, pigment distribution and high barrier properties, the anticorrosive performance of the existing styrene-acrylic binders can be enhanced. Additionally, by combining the know-how of structured particles with a new technology based on corrosion-inhibiting functionalities, further improvement of the results in SST was achieved. This was done via a built-in corrosion protection mechanism resulting in outstanding performance in salt-spray testing and good early water-spot resistance.

In the second part, minimization of the migration of corrosion causing agents was accomplished by optimizing film formation through polymer design and solvent choice, as well as minimizing water soluble components in the latex. This, and careful formulation provided superior direct-to-metal coatings. In the final part, two hybrid binders that provide protective coatings with improved barrier properties, extremely low water uptake, and excellent anticorrosion properties, even at low dry film thickness, were described. This was done by combining two different materials (acrylic polymers with either a hydrophobic polymer or an alkyd resin) during the binder synthesis. CT

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