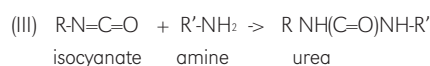
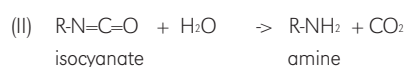
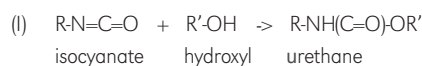


State-of-the-art of corrosion protection with waterborne polyurethane coatings

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Because of their good chemical resistance, weather stability, long-term flexibility and long service life, polyurethanes are used in a wide variety of coatings, predominantly for top coats and clear coats.

Polyurethanes are produced by the addition process from polyisocyanates and polyols. Because of the wide variety of raw materials used for these components, the resultant polyurethanes can be formulated for an enormous range of different property profiles. The most important chemical reactions are:



The reaction with water, giving off carbon dioxide (II) and the reaction with amines to produce urea groups (III) are, alongside the desired reaction (I), important secondary reactions that have to be taken into account in the formulation of polyurethane coatings.

Polyurethanes are used commercially in the form of liquid solventborne and waterborne coatings, 100 % high-build coating systems, UV and radiation-curing, air-drying and baking systems, and last but not least in powder coatings. In the case of large objects in the field of corrosion protection, oven drying and UV curing cannot be considered for practical reasons. To be able to apply air-drying coatings in thin coats with satisfactory flow and leveling properties, these are formulated with suitable solvents. There are two basic ways to produce a polyurethane film from a coating formulation on a substrate surface:

- One-component (1K), in which the polyurethane is in the form of a finished (linear) polymer. After evaporation of the solvent, a thermoplastic polyurethane film is left behind.
- Two-component (2K), in which the polyurethane is formed through a chemical reaction after the two components – the polyol and polyisocyanate – are mixed together. The reaction begins immediately

after mixing and continues for a time after the solvent has evaporated. The resultant film of polyurethane is usually highly crosslinked.

Two-component polyurethane coatings can also be formulated without solvents, but these systems are not suitable for thinner coats because of their high viscosities and flow properties. Use is also made of functional polyurethane prepolymers, which react, for example, with atmospheric moisture. A vast number of processes have been developed for effectively producing coating films from polyurethanes. The areas of application are correspondingly diverse [1].

The stricter regulations on emissions to improve health and environmental protection have induced coating manufacturers to endeavor to increasingly eliminate solvents from their coatings. In the meantime, water has proved to be the "substitute solvent" of choice, in which the binders are present in a dispersed phase and no longer as a solution. Resin producers market the appropriate coating resins as waterborne dispersions or as water-dispersible materials.

Considering the worldwide consumption of coatings in general, the changeover to waterborne coating systems has been proceeding only slowly. In many cases, it represents a technical challenge not only in terms of the properties of the coatings but also regarding the design of the equipment used by the customers to apply them. The overall share of waterborne coating materials (without binders for architectural applications) in 2005 was below 10 % worldwide, and the proportion of environmentally friendly powder coating materials [2] is equally small. However, there have been successful changes towards waterborne, in that they are now common in wood coatings and flooring, in the metal industry, e.g. cathodic electrodeposition coatings in the automotive and industrial sectors as well as waterborne OEM primers and basecoats.

In the field of industrial low-to-moderate-temperature drying systems for metal, polyurethane coatings are largely solventborne. One exception is that of commercial vehicles (rail, road, agricultural, construction and earthmoving equipment, in which

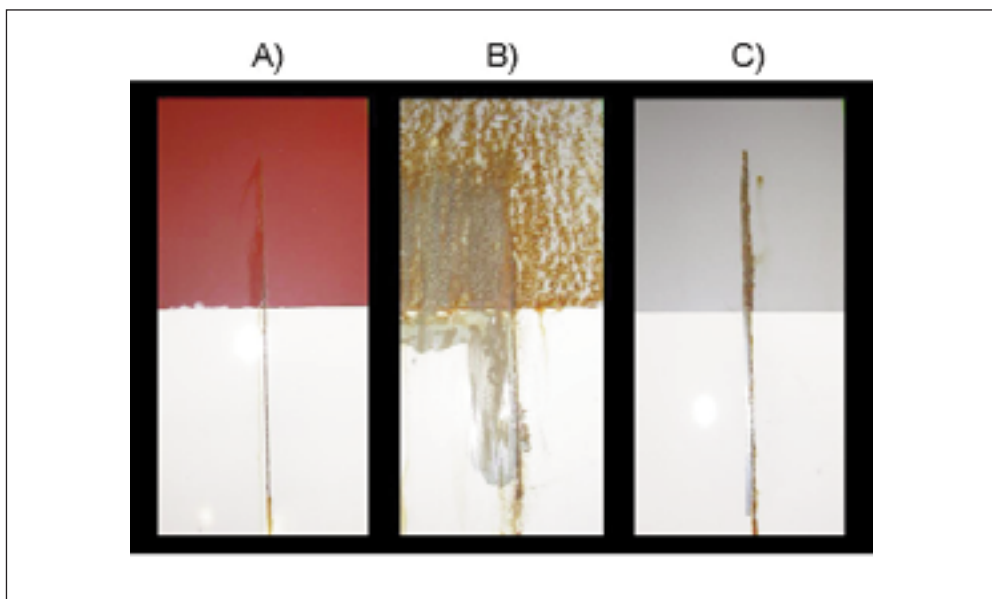


Fig. 1: Results from the salt spray test on steel panels (DIN EN ISO 9227) after 240 h. Primers: A) SBD, B) SAE, C) WB PUR 1. The primers were dried for 16 h at room temperature. Dry film thickness 45 μm . The top coat is based on WB PUR 1, also and formulated identically for all the panels.

considerable successes have been achieved in Europe with the changeover by some manufacturers to waterborne polyurethane systems [3].

This article describes air-drying waterborne polyurethane systems that can be used both in top coats and in primers, and shows why there is no real reason to delay the changeover to these environmentally friendly coatings any longer.

One-component Waterborne Polyurethane Coatings

One component (solvent based) thermoplastic polyurethanes do not provide the oxygen and water barrier effect that is needed for corrosion protection. However, unlike polyurethanes dissolved in organic solvents, polyurethanes with a very high molecular weight can be built up in a waterborne dispersion, because molecule size does not contribute to the viscosity of an aqueous dispersion. Nevertheless, polyurethane dispersions that dry purely by physical means, even with very high molecular weights, are unsuitable for corrosion protection because of their swelling characteristics and their lack of moisture and oxygen barrier properties.

One solution to this problem is to ensure adequate crosslinking in the coating film. With baking systems, this can be achieved, for example, by adding melamine resins or using blocked polyisocyanates. The co-reactants to be crosslinked must have the appropriate reactive structures such as carboxy (-COOH), hydroxy (-OH) or amine (R-NH-R').

For one-component (1K), air-drying systems, on the other hand, oxidative curing is an option, as is popular with alkyd resins [4]. Through the use of alkyd resin, diisocyanates and the incorporation of hydrophilic groups, it is possible to synthesize urethane alkyds

that are dispersible in water. Such products have been in use for a very long time and due to the urethane groups, have improved abrasion and hydrolysis resistance in the coating films [5]. Normally, these products contain co-solvents such as N-methyl-2-pyrrolidone (NMP), and do not have the same gloss as purely solvent-based alkyd resins.

More recent developments concern the reduction of the co-solvents to zero, as well as attempts to widen the range of possible applications for these systems. The product subsequently referred to in this article as WB PUR 1 is an anionic, waterborne aliphatic urethane alkyd, which is free of co-solvents, has a solids content of 45 %, contains 2.1 % OH groups calculated on resin, and is stabilized at pH = 7.2 [6]. Due to its content of hydroxyl groups, the product can also be used in waterborne two-component coating systems. The product can be formulated as a primer, a single layer coating or a top coat, and it represents the state of the art in this group of products.

Fig. 1 shows the primers formulated from conventional oxidatively drying anionic styrene-butadiene dispersion (SBD), and an anionic styrene-acrylate emulsion polymer (SAE), in the salt spray test, compared with a primer formulated from WB PUR 1 [7, 8]. The VOC of primer C) is <100 g/l.

Example B) shows that the styrene-acrylate emulsion does not pass the salt spray test and shows considerable sub-surface migration following damage to the top coat. (Due to promising results in recent developments, an improved performance of polyacrylic polymers is expected).

How do the waterborne urethane alkyds compare with each other? To determine this, various tests were carried out and compared with three commercially available, oxidatively drying polyurethane dispersions.

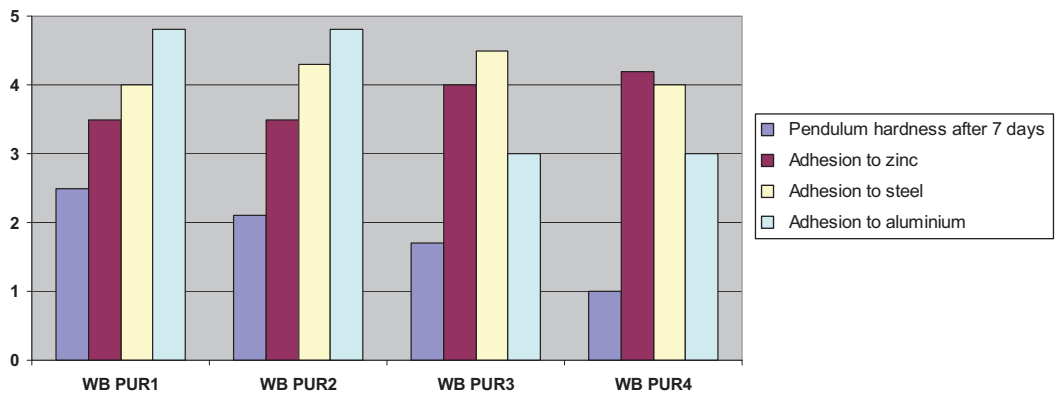


Fig 2: Comparison of waterborne urethane alkyds, formulated as primers. The index is 0-1 = very poor, 4-5 = very good (corresponds to target)

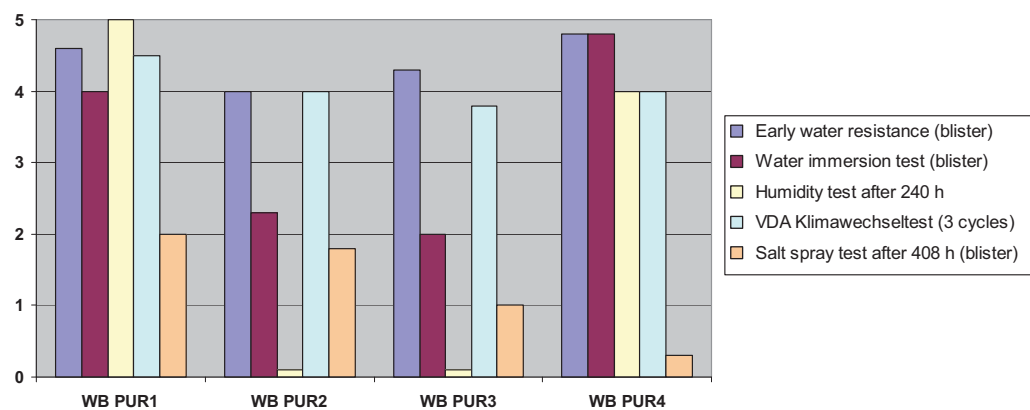


Fig. 3: Comparison of waterborne urethane alkyds, formulated as primers. The index is 0-1 = very poor, 4-5 = very good (corresponds to target)

The products will subsequently be called WB PUR2, WB PUR3 and WB PUR4. Fig. 2 shows the adhesion to various metals and the hardness of the primers. The dry film thickness is in the range of 40 – 50 µm.

Overall, the tested products are still relatively soft even after 7 days. Adhesion to the zinc and steel is good in all cases.

Fig. 3 shows the resistance to water and different environments according to various test methods. Two systems show weaknesses in the humidity test and they all generally have difficulties after prolonged exposure to the salt spray test. The overall picture shows that modern waterborne urethane alkyds can satisfy most of the requirements – with WB PUR1 turning in a balanced performance at a high level.

Two-component Waterborne Polyurethanes

Development Process

Fast drying at moderate temperatures, early readiness for use and excellent resistance properties due to high crosslinkage and urethane content have led since the 1970s to the rapid growth of two-component polyurethane coatings, especially for use as top coats in car repair finishing and large-sized vehicles.

Acrylic polyols or polyester polyols as the binder formulation (A-component) are mixed with trifunctional aliphatic isocyanates (hardener, B-component) immediately before application. The solvent content of such coatings is in the range of 35-50 %. Replacing the solvents with water was considered impossible for some considerable time, because the well-known reaction of isocyanate with water (reaction equation II) leading to the formation of CO₂ and foaming.

In 1989, around 20 years after the successful market launch of two-component polyurethane coatings, Bayer AG registered a patent for the production of coating films from a combination of hydrophobic isocyanates and aqueous polyols [9].

It was shown that, if there is adequate shear, the dispersed polyols had a sufficient emulsifier effect to finely distribute even the polyisocyanate that is not miscible with water. Fundamental investigations [10, 11] of this complex physical-chemical system from various phases and reactive components showed

- that various separate phases of polyol and isocyanate are formed,
- that, although the dispersed polyisocyanate droplets react with water, they still form a film of solid urea on the surface (reaction equations II and

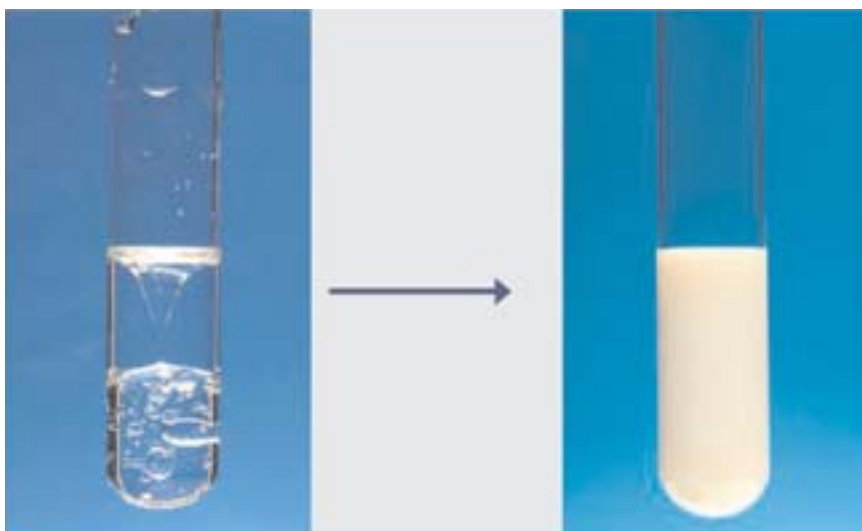


Fig. 4: HDI trimer is not miscible with water (left). Hydrophilically modified HDI trimer forms a homogeneous emulsion after brief stirring (right).

III), which protects the isocyanate from further reactions with water for some time,

- that the water evaporates relatively quickly from the wet film
- that, after evaporation of the water, a homogeneous phase of polyol and isocyanate forms in exactly the same way as a drying film from solvent formulations,

- that the best results are obtained when the isocyanate particles are as finely dispersed as possible, and
- that the reaction between polyol and isocyanate continues for some time after evaporation of the water.

A key to adequate gloss, homogeneity of the films and optimal properties is the quality of

the mixing and dispersing of the polyisocyanate. A further advance has been made with "self-dispersing" polyisocyanates to which hydrophilic groups are attached [12], cf. Fig. 4, but also with new isocyanates with very low viscosities. Common polyisocyanates are trimers of hexamethylene diisocyanate (HDI). To take account of the reaction with water, the isocyanate is generally used in a 1.5 molar excess (NCO/OH).

The following hydrophilic groups are bound to the polyisocyanate:

- non-ionic: polyethylene oxide
- $(\text{O-C}_2\text{H}_4)_n\text{-O-CH}_3$
- ionic: sulfonate, amine-neutralized $-\text{SO}_3^- \text{R}_3\text{NH}^+$

Polyether-hydrophilized polyisocyanates are state of the art, whereas the sulfonate-modified polyisocyanates are newer products. [13]. External emulsifiers can cause problems (migration, fogging, plasticizer effects), which means that internal hydrophilization should clearly be preferred. The choice of the polyisocyanates is not limited to the adducts of HDI, recent new developments enable the use of other products such as isophorone diisocyanate (IPDI) to modify hardness and

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performance. The choice of the polyol components, however, is much larger with regard to the polymer variants. As with the solvent-based two-component polyurethane coatings, polyacrylic polyols and polyester polyols have proved to be the best choice.

There are limits within which two-component waterborne polyurethane coatings can be safely applied. The pot life varies between one and several hours. The end of the pot life becomes apparent by an increase (doubling) of the viscosity. In this respect, the system differs from two-component waterborne epoxy coatings, where the end of the pot life is not obvious. The slower the reaction (formation of urethane groups), the more time the polyurethane system has to undergo secondary reactions and the greater the tendency to blistering through the generation of CO₂. On the other hand, if the drying process and the reaction take place too quickly, the coating is unable to adequately deaerate on spray application, with the result that air bubbles become entrapped and the flow and leveling properties deteriorate. With high film thicknesses, it is more difficult for the water to evaporate quickly enough. These factors thus limit the film thickness. Dry film thicknesses >100 µm still represent the biggest challenge for two-component waterborne polyurethane coatings. Slowly evaporating solvents keep the surface open and prevent skinning, which entraps the water. For this reason, most two-component waterborne polyurethane coating formulations still contain 5-10 % co-solvent.

Another new development involves what are called "activated" waterborne polyols. They have a much higher reactivity to the isocyanate groups, and are thus selectively faster than the competing isocyanate/water reaction. The result is more rapid curing but only a minor influence on pot life. With the same pot life, an activated acrylic polyol achieves comparable coating properties in half the time as an identical standard acrylate requires, and is thus even faster than a corresponding solvent-based coating [14].

Use as a Primer

While two-component waterborne polyurethane coatings are frequently used as top coats and clear coats, they are rarely used as primers compared with the analogous epoxies. One of the reasons for this is that, in the primer, the change from solvent-based to water-based epoxy is regarded as a logical system follow-up. Furthermore, the use of two-component polyurethane coatings was a bit limited due to their price. The situation has changed because

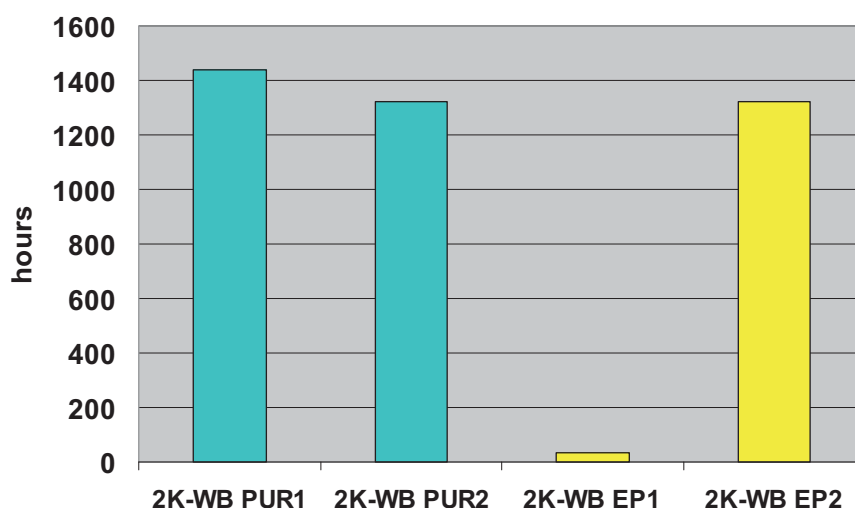


Fig. 5: Water immersion test - time to first blistering

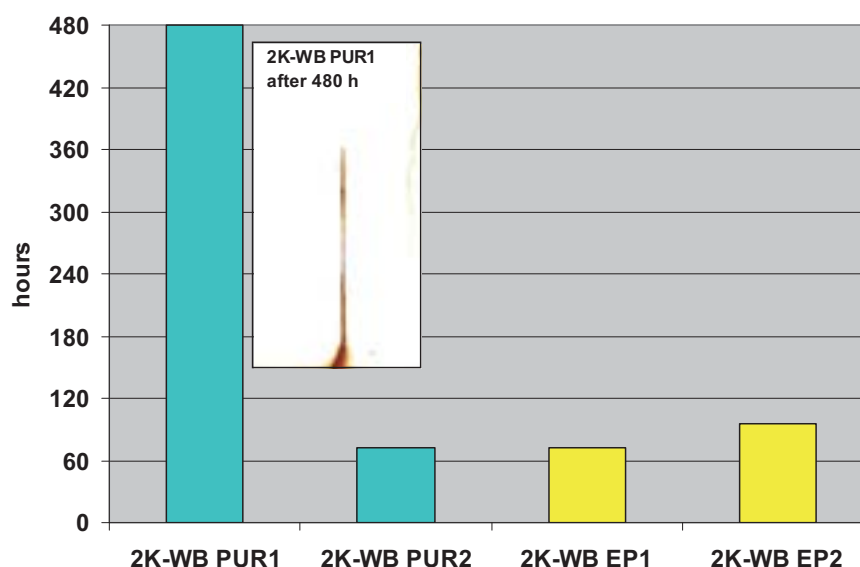


Fig. 6: Salt spray resistance - time to first blistering

two-component waterborne polyurethanes now also boast an outstanding set of properties as a primer. So what can these systems do for corrosion protection?

Most recently, progress has been with the aqueous polyols. Lightfast acrylic polyols with a high OH content for optimal crosslinkage enable the use of a product of this kind both for primers and for high-quality top coats with easy-to-clean properties. One such product was recently introduced onto the market with an OH content of 5.0 % calculated on solid resin, 41 % solids, and a co-solvent content of 7.6 % [15].

A primer formulated in this way and subsequently called 2K-WB PUR1 was compared with other commercially available systems [16]. The figures 5 and 6 show just some of the results obtained with waterborne two-component primers:

2K-WB PUR1	state-of-the-art polyurethane
2K-WB PUR2	commercially available polyurethane system
2K-WB EP1	commercially available epoxy system
2K-WB EP2	commercially available epoxy system

The primers were dried for 10 days at room temperature; the dry film thickness was approx. 60 micrometers. The pot life was 1-2h with the exception of 2K-WB PUR2 (6h). T3 drying times (tack-free) differed: Fast with 2K-WB PUR1 (1.5 h) and 2K-WB 2 (2 h), moderate with 2K-WB EP2 (3 h), and very slow with 2K-WB EP1 (6.5 h).

Apart from 2K-WB PUR1, all the systems show particular weaknesses in the salt spray test (Fig. 6). In the water immersion test in Fig.

5, one of the epoxy primers also fails very early. In the condensed water test (no diagram), only 2K-WB PUR1 withstands more than 1,400h, while all the other systems fail after only 240-360h.

The surprisingly poor results of the two-component waterborne epoxy primers were confirmed by other tests to establish their suitability for military vehicles [17]. Here, too, not all polyurethane systems are suitable for these applications, as the results showed.

Quick drying and outstanding resistance properties can, however, be achieved with two-component waterborne polyurethane coatings if a suitable polyol component is selected. Formulations of this kind are also competitive in corrosion protection.

Conclusions

If suitably formulated, very good results can be obtained in corrosion protection with one and two-component waterborne polyurethane coatings. Especially for demanding applications, the two-component systems would seem to be particularly suitable. With excellent practical experience behind them as top and clear coats, the door is wide open for high-quality polyurethane-based primers. ■



2K waterborne polyurethane applied by automatic spray to crane components.

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