Coatings with Self-Cleaning Properties

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Summary: The issue of self-cleaning significantly gained popularity due to the work of Barthlott and coworkers on the so called "Lotos-Effect®". They found out, that the cleanliness of the Lotos leaves originates from a combined effect of surface topography and hydrophobicity. The symbol of the beautiful Lotos flower as well as the fascination of surfaces being cleaned without any manual activity, simply by a rain shower, has since then stimulated the fantasy of many researchers. Our vision is to copy this mechanism from mother nature and to implement it into coating systems in such a way, that conventional application techniques, e.g. spray-coating, can be applied without the necessity of further process steps like e.g. soft lithography. Three different approaches will be presented in this paper. Roughness and contact angle measurements have been used to quantify the self-cleaning properties.

Keywords: coatings, structure, surfaces

Introduction

„Self-cleaning" is a prominent example for a desired property of a whole class of high-performance coatings, namely *functional coatings*. This term classifies systems, which posses besides the classical properties of a coating, i.e., decoration and protection, an additional functionality. Depending on the actual application, additional functionality of a coated surface can be manifold, e.g., soft-feel or soft-touch haptics for interior car parts, easy-to-clean (anti-graffiti) for storefronts or anti-fouling for ship bodies. Although the range of applications as well as the underlying chemistry is diverse, all these systems have in common a very specific benefit, which in each case provides an answer to an existing and well defined demand.

The issue of self-cleaning significantly gained popularity due to the work of Barthlott and coworkers on the so called "Lotos-Effect®" [1]. They found out, that the cleanliness of the Lotos leaves originates from a combined effect of surface topography and hydrophobicity. The symbol

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of the beautiful Lotos flower as well as the fascination of surfaces being cleaned without any manual activity, simply by a rain shower, has since then stimulated the fantasy of many researchers. From a pure scientific point of view, however, the influence of roughness (also in combination with hydrophobicity) on water repellency was already known much earlier [2] and could also be understood on a sound thermodynamic basis [3, 4].

Our vision is to copy this mechanism from mother nature and to implement it into coating systems in such a way, that conventional application techniques, e.g. spray-coating, can be applied without the necessity of further process steps like e.g. soft lithography. The decisive challenge in reaching this target is of course a coating formulation which is capable of building up a suitable microstructure just on its own. In comparison, adjusting the hydrophobicity of the surface is much more straightforward. Three different approaches for coatings leading to microstructured surfaces will be elucidated. They are a) use of inorganic fillers, b) use of polymeric together with inorganic fillers and c) thixotropic textured coatings. These systems are compared to a conventional 1K automotive clearcoat.

Thermodynamics of contact angles on rough surfaces

From daily experience we know that a drop of water deposited onto a coated surface will form a sessile drop. The angle formed between the liquid-vapor interface and the liquid-solid interface at the solid-liquid-vapor three-phase contact line is conventionally defined as the *contact angle*. Despite the apparent simplicity of sessile drops on solid surfaces, contact angle phenomena are rather complex. Minimizing the overall free energy of a system consisting of a liquid in contact with a solid yields the Laplace equation of capillarity [5]

$$\gamma_{lv}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)=\Delta\rho g z+c=\Delta P \tag{1}$$

and Young's equation [6]

$$\gamma_{lv}\cos\theta_e=\gamma_{sv}-\gamma_{sl} \tag{2}$$

where γ_{sv} is the solid-vapor interfacial tension, γ_{lv} is the liquid-vapor interfacial tension, γ_{sl} is the solid-liquid interfacial tension, θ_e is the equilibrium contact angle, R_1 and R_2 are the principal radii of curvature at a point of the liquid surface, $\Delta\rho$ is the density difference between the liquid and vapor phase, g is the acceleration due to gravity, z is the ordinate of a point of the liquid surface at which the principal radii of curvature are R_1 and R_2, c is a constant and ΔP is the capillary pressure or pressure of curvature.

While the Laplace equation essentially describes the shape of the liquid-vapor interface away from the solid-liquid and solid-vapor interfaces, the Young equation involves properties which are a function of the solid surface, i.e., γ_{sv} and γ_{sl}. The derivation of eq. (2) assumes that the solid surface in contact with the liquid is smooth, homogeneous, isotropic and non deformable.

On rough solid surfaces Wenzel [7] recognized that Young's equation may not be a universal equilibrium condition for the physical interaction between a solid and a liquid. He argued, essentially, that if the solid surface is rough, the interfacial tensions γ_{sv} and γ_{sl} should not be referred to the geometric area, but to the actual surface area. If we let

$$r = \frac{actual\ surface\ area}{geometric\ surface\ area} \tag{3}$$

this leads to the so called Wenzel equation

$$r(\gamma_{sv} - \gamma_{sl}) = \gamma_{lv} \cos\theta_W \tag{4}$$

where θ_W may be called the Wenzel contact angle. Equation (4) was also derived by Good [3].

In a thorough thermodynamic analysis Li and Neuman [4] have shown, that although θ_W is indeed the equilibrium contact angle θ_e, it is not accessible in experimental measurements. According to their analysis, a large number of metastable states of the free energy are existing for liquids on rough solid surfaces which correspond to the same number of metastable contact angles. Only the largest and the smallest contact angle can be observed experimentally. The former is referred to as the advancing contact angle (θ_a), while the latter is called receding contact angle (θ_r). The difference between θ_a and θ_r is the so called contact angle hysteresis, which may be conveniently measured by first advancing and then receding a liquid drop over a solid surface. Thus, for practical purpose, contact angle hysteresis measurements are best suited for quantification and evaluation of water repellency on structured surfaces.

The extraordinary water repellency, which can be observed on rough surfaces like e.g. lotos leaves, originates from a combined effect of surface structure and hydrophobicity, i.e. low surface tension of the solid, γ_{sv}. In this case one can observe an "air-cushion effect", if the water droplet "rests" on the peaks of the structures and is not able to penetrate into the valleys. Based on the theory of capillarity, i.e. taking into account eq. (1) and (2), it is possible to calculate the size of suitable surface structures for ideal geometries. This was done by Dettre et al. [2] for two cases. The first one has been a surface having holes of the shape of cylindrical capillaries, and the second one has been a surface consisting of vertically oriented cylinders. They derived the following equations for the capillaries

$$P = \frac{4\gamma_{lv}}{c}\cos\theta_a \tag{5}$$

and the cylinders, respectively.

$$P = \frac{\pi d\gamma_{lv}\cos\theta_a}{0.8660b^2 - (\pi/4)d^2} \tag{6}$$

Where P is the pressure, which is required to force water into the capillary (or between the cylinders, respectively), γ_{lv} is the liquid-vapor surface tension, c is the diameter of the capillaries, θ_a is the advancing contact angle, d is the diameter of the cylinders and b is the center-to-center distance between cylinders.

For this ideal geometries, Dettre et al. have calculated the maximum structure size for a self-cleaning wax surface, i.e., a very hydrophobic surface (comparable to the lotos leaves), of about 300 microns. Although the surface structures in practice will differ significantly from the situation described by eq. (5) and (6), the values calculated with these equations provide at least a valuable orientation and a good starting point for further experiments.

Materials and Methods

An overview of the different textured coating systems is given in table 1.

Table 1. Overview of textured coatings

#	Resin	Roughness due to	Hydrophobicity due to
1	OH-functional Polyacrylate Melamine X-linked	Inorganic particles	Fluor additive
2	OH-functional Polyacrylate Melamine X-linked	Inorganic and organic particles	Fluor additive
3	OH-functional Polyacrylate isocyanate X-linked	Thixotropic binder	Wax additive
4	OH-functional Polyacrylate Melamine X-linked	---	---

Roughness measurements

The roughness of the coated surfaces was measured with a Hommeltester T4000 equipped with a TKPK100 sensing device on an area of 2 mm x 2 mm with a velocity of 0.15 mm/s.

Contact angle hysteresis measurements

The contact angle hysteresis was measured with a G2 instrument from Kruess, using water as test liquid (LiChrosolv (Merck), water for chromatography). The needle of the syringe was kept in the sessile drop from above during the whole experiment. The drop was first slowly advanced over the surface by pushing additional water through the needle and then slowly receded by withdrawing the liquid. Simultaneously the contact angle was measured by aligning a tangent to the drop profile by means of the software of the G2 instrument.

Results

Roughness measurements

Fig. 1 shows the results of the roughness measurements. The surface of the conventional 1K clearcoat (#4) is, as expected, extremely smooth. Only a little weaviness with maximum heights well below 1 μm is present. In contrast, the surfaces of the other three systems are very rough. While the lateral structures of these three coatings are in the same order of magnitude (between 50 μm to 300 μm), the heights of the peaks are very different. As can be seen from the scale of the z-axis, the peak-to-valley height is about 10 times larger for systems #1 and #2 as compared to coating #3 (about 100 μm vs. about 10 μm).

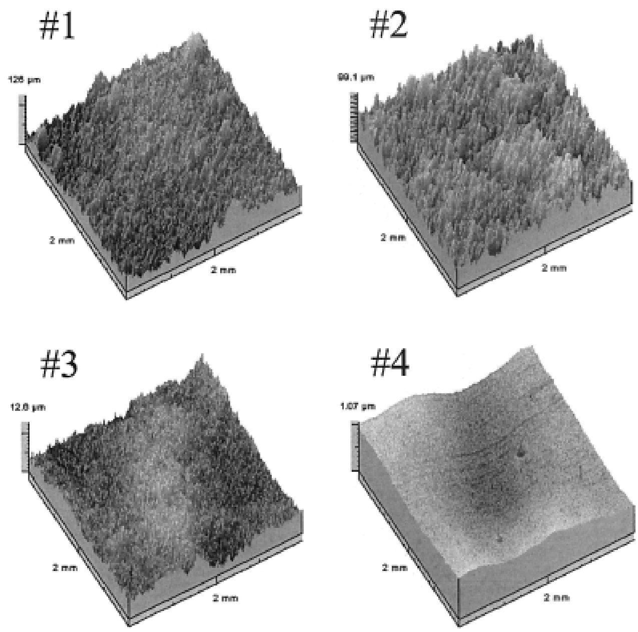

Figure 1. Surface roughness of the four different coatings

Contact angle hysteresis measurements

A typical result of a contact angle hysteresis measurement is shown in Fig. 2 (system # 3). It can be seen that the water drop advances with a fairly constant contact angle of about 100 ° over the surface. After 50 measurements, the water has been withdrawn from the drop. While the drop is receding over the surface, the contact angle initially decreases by about 30° and reaches then a constant value of about 70°.

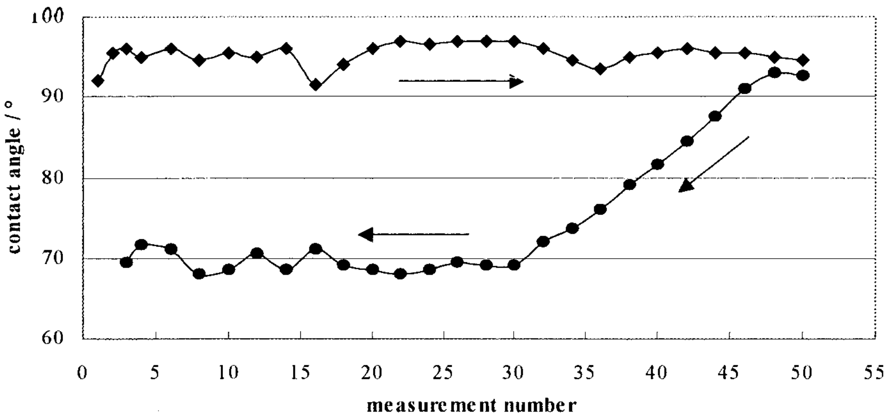

Figure 2. Typical contact angle hysteresis measurement (coating #3). The squares are advancing and the circles are receding contact angles.

The contact angle data of all coating systems are given in table 2 and typical images of receding contact angles are shown in Fig. 3.

Table 2. Results of contact angle hysteresis measurements

Coating #	θ_a [°]	θ_r [°]
1	140	140
2	140	130
3	102	70
4	86	20

(θ_a: advancing contact angle, θ_r: receding contact angle)

The behaviour of system #4 is typical for an automotive clearcoat without any self-cleaning properties: The advancing contact angle is relatively small (about 90 °) and the hysteresis is very pronounced. Due to the extremly low receding contact angle of about 20 °, traces of water remain on the surface. Dust or dirt will not completely be washed away by a rain shower.

Systems #1 and #2, in contrast, posses impressive self-cleaning properties, which are comparable to the leaves of the lotos flower. Both systems show extraordinary large advancing contact angles and virtually no hysteresis. Water drops take up dirt from the surface and roll off easily. System #3 shows an intermediate behavior: The advancing and especially the receding contact angle are considerably larger than on the standard (system #4), but smaller as for system #1 and #2.

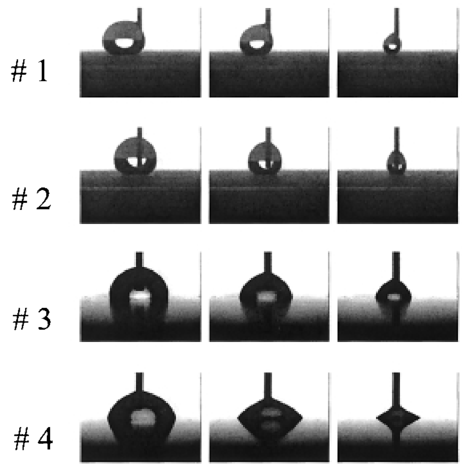

Figure 3. Receding contact angles for coatings systems #1-4.

Conclusions

It is possible to formulate coatings with extraordinary self-cleaning properties, which are applied simply with a spray gun. The results for system #1 and #2 have shown, that these surfaces are sufficiently hydrophobic and capable to build up a suitable microstructure. However, these structures are rather fragile. The mechanical stability is not yet sufficient for technical applications. Another approach was shown with system #3: This system has much better self-cleaning properties than the standard (#4) and the mechanical stability is ok.

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