Chemically active coatings

Several types of surface-functional coatings perform their functions via particular physical properties of their top surface, leading to, e.g., a low free surface energy, good chemical, light and thermal resistances, or excellent mechanical properties. These have been described in a previous article [2]. Here, functional coatings that act through specific chemical, photochemical, or biochemical properties of their top interface (film/air) are reviewed, such as self-cleaning, pollutant destructing, anti-bacterial, and antifouling coatings.

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There are several types of chemically active organic coatings, which rely on controlled chemical (electrochemical, biochemical, photochemical) processes. Because of growing environmental concerns, their efficiency and toxic characteristics deserve special attention and, in the majority of cases, are the objects of corresponding regulations. Traditional types of chemically active coatings (anticorrosive, rust-conversion, fire retardant, wood bio-protecting, and antifouling coatings) has meanwhile been extended by a number of relatively new types.

Topographically, chemically active coatings can be divided into the three major categories:
- One group includes systems, where chemical transformations take place inside the bulk of the coating films (e.g., intumescent coatings). Coatings belonging to the second group reveal their activity across or near the adhesion (film/substrate) interface. Thus, anticorrosive coatings control electrochemical processes in metal substrates, which proceed near the adhesion interface. Rust-conversion coatings react with the rust, and bio-protecting coatings preserve wood, while across at the film/substrate interface.
- This article discusses the third group of coatings, which is gaining more and more importance over the last decade, namely those which act via various chemical transformations on or near the top (film/air) interface. In particular, these are self-cleaning, pollutant destructing, anti-bacterial, and antifouling coatings.

General mechanisms of action

Chemically active surface-functional coatings use several different mechanisms. The active (reaction) zone can be located either directly at the film/air interface (requiring the reagents to diffuse from either one or both sides), or they can be located in the near-interface layer. If required, energy is supplied from external sources (e.g., sunlight, or heat).

Reaction products can be removed from the surface either through natural action (wind or rainwater), or mechanically. Catalytic (catalyzing) coatings act via a catalyst fixed on (or near) the top surface of the coating. This is shown schematically in Figure 1a. The chemical reaction takes place when the reagents approach from the ambient, wet or become absorbed by the surface. Catalytic coatings are usually formulated containing the catalyst (for example, TiO₂ anatase pigments). Alternatively, coatings can be post-treated to introduce a catalyst material into the top surface layer of the film. Pollutant destruction coatings use this scheme of function.

Figure 1b illustrates another mechanism: The top coating interface is approached by the reagents bilaterally - both from the ambient and from the bulk of the coating film towards the interface, where a chemical (e.g., bio-chemical, photo-chemical) reaction occurs. Anti-microbial and conventional antifouling coatings follow this scheme.

Finally, chemically reactive coatings can feature a so-called controlled erosion mechanism (Figure 1c). Here, the top layer of the coating is a reactive zone containing a reagent (or reagents) and possibly also a catalyst, which is subjected to a gradual destruction and removal. Self-polishing antifouling and self-cleaning (chalking) atmospheric coatings use this mechanism.

Surface cleanability

Several approaches are in use to achieve clean top surfaces of organic coatings during their service in polluting environments. They can be distinguished by focusing on different aspects of dirt (contaminants) attachment to and detachment from the coating surfaces. In particular, they are defined as "dirt pick-up" and "surface cleaning", respectively. The following surface properties are believed to determine the coating's dirt-pick up and cleanability [1]:
- the free surface energy (prevailing factor)
- surface morphology
- surface electroconductivity

Chemical inertness, durability, and surface chemistry should also be taken into consideration [2], in particular because the surface molecules of any binder material are prone to change their composition under the action of atmospheric oxygen, moisture, and sunlight.

The complex effect of reaching non- or low-contaminated surfaces can be achieved by:
- preventing contaminants from attachment,
- imparting so-called release properties to the surface,
- decomposition of contaminants at the coating surface to form volatile or easily removable products, and
- conversion of the top coating material (binder, pigment, or additive) into a substance capable to interact with contaminants and promoting their detachment.

The first two approaches are based on physical processes, while the last two involve chemical reactions (Figure 2). Each of these functional qualities, however, has its limits in the practical application [3]. Besides, easy-to-clean (a cleaning is still needed) and self-cleaning properties (a clean surface is provided without any additional manipulation) have to be distinguished.

Preventing surface contamination (low dirt pick-up, easy care)

Specific conditions of use usually dictate the approach to prevent dirt pick-up and promote cleanability. Exterior (façade) architectural coatings collect the dirt mainly as a deposit left by rainwater. Therefore, façade coatings can be formulated with additives, which would minimize the effect of the water leaving deposits on the surface - by making them very hydrophobic (the surface repels the water). As for interior coatings, providing them with a sufficient surface electroconductivity (e.g., by using ionic surfactants, quaternary ammonium salts, or alkyl sulfonates) can significantly reduce the deposition of dirt.

These traditional approaches are not the only viable ones. According to Akzo Nobel Nippon Paint, specific combination of hydrophilicity and low surface energy in a single topcoat for coil coating offers a very pronounced easy-to-clean effect [4]. The ability of organic coatings to be de-contaminated from radioactive contaminants can be increased, when the same binder type is used with a higher cross-linking density [5].

Release coatings (dirt repellent, easy-to-clean, self-cleaning)

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This mechanism is based on specific surface properties of selected polymers, possessing a combination of low free surface energy and chemical inertness (in particular, this is characteristic for fluoro-, or silicone containing or modified polymers). The release properties of a matrix polymer allow to prevent the attachment of, e.g., dirt or grease particles and provides the easy removal.

For instance, anti-graffiti coatings can be formulated based on graft co-polymers of acrylic resins and silicone oligomers [6]; they combine surface hardness, inertness and low free surface energy. Dirt repellent coatings based on the "Lotus-Effect" or Bionic-Effect [7,8] make use of a combination of a specific surface topography and hydrophobicity, which makes them especially effective against solid contaminants. The specially designed surface morphology prevents particles from getting into intimate contact with the surface (so that significant adhesive forces can not be developed), whereas the low free surface energy and consequent hydrophobicity renders the surface water-repellant. Thus, even small amounts of water placed onto such surfaces are not able to wet the surface and spread on it. Instead driven by the surface tension, it forms droplets which wet the contaminating particles and detach them from the solid surface.

**Controlled erosion (self-cleaning) coatings**

Their functionality is based on the removal of surface contaminants jointly with a part of the surface coating material, which is destroyed, dissolved, or subjected to other physical or chemical processes, which transform it into an easily detachable and removable substance. Self-polishing antifouling coatings in particular utilize such mechanisms.

**Pollutant destructing coatings**

Perhaps, the most sophisticated approach to coating cleanability is based on a possibility for spontaneous chemical or bio-chemical destruction of surface contaminants in contact with an appropriately activated coating surface.

**Bio-active coatings**

Micro-organisms - bacteria, fungi (moulds and yeasts) and algae - are minute organisms, which have very simple requirements for growth. Many coatings need to be capable of destroying such species or at least prevent their growth, i.e. to possess a biocidal effect. In the majority of cases, however, the goal is to prevent biological destruction of the coating films in service and/or susceptible substrates (wood, for example) [9].

Since any biocide is essentially toxic, paint formulators always seek approaches to minimize their use by enhancing their performance. Novel technologies have been developed for formulations of architectural, wood, or antifouling coatings, where silica or aluminosilicate (zeolite) structures are used as carriers for biocides [10].

**Antifouling Coatings**

Marine conditions are specifically damaging for various materials, including metals and concrete, caused by the collective actions of a humid and chemically aggressive atmosphere, salty water, sunlight, and various marine organisms. Bacteria cause microbiologically influenced corrosion of marine structures, while algae and fungi destroy coatings. Alkyd and even vinyl-based coatings typically show insufficient resistance against bio-corrosion; chemically cured epoxy coatings in the majority of cases exhibit sufficient durability [11].

Another damaging effect is fouling, i.e. an unwanted growth of biological material on the objects immersed in water (underwater areas of sea constructions, ship hulls, etc.). It can be divided into two main categories, micro- and macrofouling. Microfouling consist mainly of diatoms and bacteria (species which individually cannot be seen by the naked eye, but when attached are observed as a slimy layer). Macrofouling can be divided into animal-caused (barnacles, tubeworms, bryoanans) and plant-caused fouling (algae) [12].

Fouling decreases the speed, maneuverability and range of ships, and raises propulsive fuel consumption by as much as up to 30% [13]. Barnacles, algae and tubeworms are the principal forms of fouling on ocean-going vessels, while mussels, hydroids, tunicates and bryoanans are prevalent when the ship spends protracted periods at dockside [14].

Antifouling coatings present a typical example of bio-chemically active surface-functional coating. There are several major types of antifouling paints in use today (utilizing different modes of action), generally falling into the two categories: biocidal and non-biocidal systems.

**Biocidal Antifoulings**

The group of biocidal antifouling coatings includes:

- conventional (contact leaching, soluble matrix-type), advanced (insoluble matrix), self-polishing copolymer systems (TBT-based, types, banned from application after 2003, and TBT-free types, based on alternative metal-containing polymers and their combinations with other biocides), polishing/ablative (combined) systems, and so called passive antifouling systems - non-stick/easy-to-clean coatings [15,16].

**Self-Polishing Coatings (SPC)**

These coatings are based on a tributyltin(TBT)-containing copolymer binder (TBT methacrylate and methyl methacrylate copolymer), usually together with co-biocides (e.g. cuprous oxide, diethiocarbamates) allowing to resist a diversity of marine organisms (lifetime up to 5 years). The TBT-binder hydrolyzes in seawater at a constant rate, releasing TBT. The copolymer resin becomes water-soluble as soon as the TBT has been hydrolyzed, and remains intact with a portion of a co-biocide (Figure 3). Seawater movement against the ship's hull polishes off the hydrolyzed reminder of the binder (Figure 4), thereby smoothing the surface, preventing a growing fuel consumption [12].

TBT-free SP antifouling coatings based on copper and zinc acrylate copolymers have recently been introduced into the market [17,18]. They react with sodium ions in sea water in a reaction analogous to TBT-SPC copolymers, releasing the biocides (Cu and Zn oxides, respectively) incorporated into the resin, and producing soluble polymer molecules on the coating surface. Another perspective approach is based on the use of natural non-polluting biocides [19].

**Non-Stick Antifoulings**

Non-stick antifouling coatings, using fluoropolymers, silicone and other low surface energy polymers as binder resins, are considered the most promising solutions that act completely without toxic biocides. To-date, such surfaces do accumulate fouling, but their attachment is relatively weak [20]. Poor abrasion resistance and reduced adhesion to conventional coatings inhibit the use of silicone resins in non-stick antifoulings, while their fluorine-containing counterparts promise non-toxic solutions in the near future.

**Pollutant destructing coatings (PDC)**

This coating type achieves the chemical self-cleaning from dust-like atmospheric contaminants (deposits) by its chemical decomposition. The PDC subjects surface
contaminants to oxidative destruction by means of the collective action of atmospheric oxygen and sunlight, activated by a catalyst incorporated into the coating’s surface. Practically, however, PDC use a combined approach, when a suitable catalyst (chemical approach) is incorporated into a low free surface energy polymeric matrix (physical approach) [21].

**Hygienic Coatings**

Anti-microbial (hygienic) coatings are formulated to destroying microorganisms (mainly bacteria) on the film/air interface bio-chemically. For instance, nanoparticle titanium dioxide, coated with a fine layer of silver, has a long-term action as a biocidal substance against various microorganisms [22].

**References**

[1] M. Krupers. ECJ 10/00, p. 36.

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-> Prof. Vladimir V. Verkholantsev was born in 1937 in St. Petersburg. He graduated in chemical engineering and started his career as a technologist in a paint factory. Upon receiving his PhD in 1965 and Dr. Sci. in chemical engineering in 1970 he became a senior research chemist and then associate professor at the Lensovet Chemical Technology Institute in St. Petersburg. Later, he was appointed full professor at the Building Engineering Institute, then professor and director of department at the Coating Research Institute in Moscow. He joined Tambour Ltd. in Israel in 1991 as head of the research group. At present he is a freelance consultant.
Figure 1: Surface-reactive coatings schemes
Figure 2: Easy-to-clean (a,b) and self-cleaning (c,d) coatings (schematic)
Figure 3: Self-polishing antifouling coating (schematic cross-section)

Figure 4: Hydrolysis reaction of TBT-copolymer in sea water