CHAPTER 7

Waterborne functional paints to control biodeterioration

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Contents

1. Introduction

Coatings are generally defined as any material (usually liquid) that may be applied as a thin continuous layer to a surface [1]. Paint is a term traditionally used to describe a specific dispersion system constituted by pigments, binder(s) (polymer or resin), solvents, and additives. These pigmented systems are designed for application to a substrate as a thin layer which is converted to an opaque solid film after application unlike of lacquers or varnishes [2,3]. Therefore, paint is any pigmented coating [3].

Coatings are usually applied as multilayered systems, each layer performing a specific function. Mostly these systems are used for decorative and protective purposes, but depending on the surface to cover and the environmental conditions in service, additional properties are required. Examples of these films with additional functionalities, known as functional coatings, are self-cleaning, easy-to-clean (antigraffiti), self-healing, anti-corrosive, hygienic, and antifouling [4−6].

The protective action afforded by paints is mainly due to a barrier effect that blocks the passage of water into and through the substrate and delays the entrance of aggressive agents. The decorative action is because paints improve the appearance and smooth the surfaces. To obtain functional coatings, paints incorporate especial pigments or additives to provide functionality (hydrophobic-, hydrophilic-, self-cleaning, and antimicrobial surfaces).

Organic solvent-borne paints cause atmospheric pollution as the paint dries or cures. Moreover, organic solvents are flammable, explosive, of unpleasant odor, and sometimes toxic [7]. Waterborne paints, which have water as volatile compound, are more desired because they are environmentally friendly, and some of their strengths are easy cleanup, low odor, nonflammable, low yellowing, and quick recoatability [8,9]. However, these paints suffer from a number of deficiencies, such as longer drying time (especially in high humidity environment), low gloss, poor hiding power, poor wet and dry adhesion, poor water and alkali resistance, and more biodeterioration when compared with solvent-borne paints [7,8].

Biodeterioration of a complex product such as paints, whereby microorganisms manage to degrade their components, depends on many factors where the most important is the amount of water available in the material [10]. The presence of microorganisms on a paint film is undesirable not only because of defacement they produce but also for the effect in indoor environments due to the release of, for example, spores, microbial fragments, allergens, volatile organic compounds, and mycotoxins. Air quality inside buildings has a profound impact on population because people spend most of their time indoors [11]. According to the World Health Organization, the excess of these agents in internal environments is a danger to human health, and for this reason, the microbiological growth must be either eliminated or minimized [12].

Taking into account the weaknesses and strengths of waterborne paints, they are worldwide used on walls, ceilings, and metallic subtracts as functional antimicrobial and anticorrosive coatings, respectively. This chapter will focus on the study of waterborne paints and the advances in the control of biodeterioration through functional strategies.

2. Waterborne coatings considerations

Paint consists, mainly, of solvents, resin, pigments, and additives, which is resumed in the scheme of Fig. 7.1 [7,13]. Solvents make coating
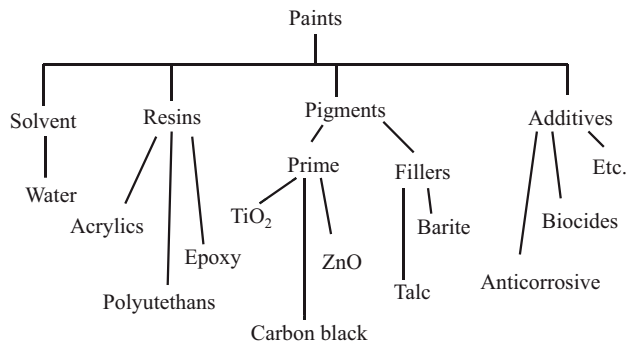
Figure 7.1 Scheme of main components of paints.

application possible and enable the processing of the paint during manufacture and film formation. Solvents control many application and appearance properties of the coating, including binder solubility and miscibility, dispersion stability, application viscosity, drying time, and film leveling [14]. In the case of waterborne coatings, up to 80% of the total solvent is water [15]. Water-soluble alcohols and cellosolve solvents can be present, in minor amount, to enhance substrate wetting, paint flow, and leveling [16,17].

As the paint dries, the aqueous solution is transformed from a dispersion of polymer particles in a continuous water phase to a dry polymer film [18]. In general, three different stages of the film formation process are recognized: (1) evaporation of water and particle ordering; (2) particle deformation; and (3) interdiffusion of polymers across particle—particle boundaries [19].

The resin is the film forming material and establishes most of the chemical and physical properties of the paint, such as adhesion (to the substrate and among paint solid components), mechanical hardness, scratch and scrub resistances, and surface slip.

Bieganska et al. [7] classified waterborne paints depending on the size of the polymer particles they contain as (1) true solutions (<0.01 μm), (2) dispersions (from 0.01 to 0.1 μm), and (3) emulsions (from 0.1 to 1.0 μm). Paul [9] classified coatings in a similar way: (1) water-soluble or reducible, (2) colloidal or water-solubilized dispersions, and (3) aqueous dispersions or emulsions. Differences between these groups are important in the physical and mechanical properties and thus provide a considerable formulation range for coating chemists [9].

Water-soluble paints are based on solutions of binders in water. Polyesters, epoxy, and modified alkyd resins are generally used as, for example,
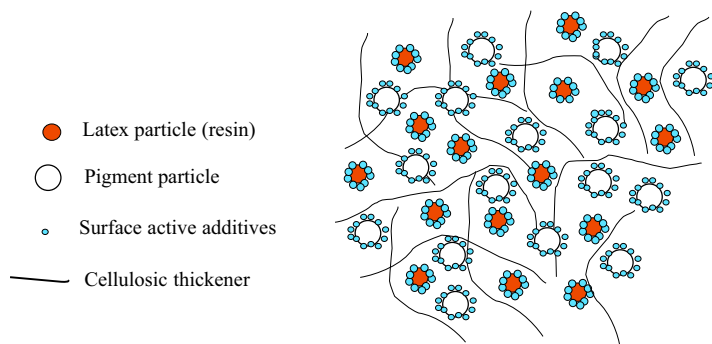
Figure 7.2 Graphic representation of a generic and basic waterborne paint before being applied.

primers for appliance industries [20,21], temporary coatings, or coatings for electrodeposition applications [9]. Aqueous dispersions or emulsions (latices), on the other hand, are used as architectural paints; a representation of the basic components of these can be seen in Fig. 7.2 [22,23].

According to Klippstein [24], waterborne epoxy coating can be categorized as follows: (1) Type I systems based on liquid epoxy resin manufactured from the diglycidyl ether of bisphenol A or bisphenol F. The amine hardener is usually an emulsifier too. (2) Type II waterborne epoxy systems based on much higher molecular weight epoxy resins, which tend to be solids at room temperature. Epoxy resins cure by chemical reaction with amines or amide and they are incorporated in anticorrosive paints with good results [20,25–27].

Kurt et al. [28] prepared water reducible alkyd resin containing different amounts of colloidal silica. Their assays showed that the coatings have excellent water, acid, and salt water resistance.

According to Schwartz [29] and Baumstark [29], acrylic copolymer dispersions can be classified as straight acrylic compounds or as acrylic/styrene compounds. In the past few years, new composite acrylic resins have been introduced in interior paints. These composites include different acrylic polymer blends, addition of styrene, silanes, or alkyd polymers [30–33].

Waterborne urethane dispersions are also used as resins in coatings. They are prepared in a two-pack system to be mixed just before using. The system includes a polyurethane polyol dispersion in water and an easily dispersible hydrophilically modified polyisocyanate [34,35].

The solvent and the resin form the vehicle.

The pigments are, for the most part, inorganic compounds, such as oxides or silicates. Pigments are any particular matter that is insoluble and unaffected by the vehicle [3,36]. Prime pigments with refractive index higher than one of the resin (>2.0) give color and opacity to the paint [3]. Among these pigments are titanium dioxide, carbon black, antimony oxide, zinc sulfur, and zinc oxide [37,38].

One of the disadvantages of TiO_2 is its UV activity [37]. However, Wojciechowski et al. [39] studied the UV stability of TiO_2 (rutile and anatase crystalline structures) in different binders. They showed that despite the markedly differences in photochemical properties of the two TiO_2 polymorphs, their effect on photostability of the binder films at low loads (1% w/w) is very similar and rather minor [39].

Extender pigments or fillers are transparent or semitransparent white or gray pigments, but they impart desirable specific properties such as aid sanding, control sheen levels, improve abrasion, affect rheology, and contribute to hide flat paints [3,40]. Some of the most important ones are precipitated calcium carbonate, barium sulfate, different iron oxides, and talc, with refractive index between 1.5 and 2.0.

Other extenders have refractive index lower than 1.5, and they do not contribute to the opacity of the paint. These extenders are natural calcium carbonate and dolomite (a natural mineral mixture of calcium carbonate and magnesium carbonate). The use of dolomite is restricted in acid–based vehicles because it reacts with them; however, it is used as buffer for certain waterborne paints, as it reduces chalking.

Acicular and lamellar extender pigments can act as mechanical reinforcement and thus improve the mechanical and barrier properties of paints [41]. Among these pigments, talc, wollastonite, and mica are the most important ones [36,42,43].

Clays are also important [44]. Kaolin or china clay allows cost reduction by extending/reducing the amount of TiO_2 [45]. Wollastonite, on the other hand, provides reinforcement in coatings, reduces resin demand, and improves bonding between minerals and resin [45].

As TiO_2 is one of the most expensive pigments in paint composition, several attempts were done to diminish its content without affecting the hiding power or pigment volume concentration (PVC). These attempts include incorporation of precipitated calcium carbonate with selected particle size and distribution or calcined kaolin [40,43−46].

Traditionally, the particle size of pigments is around 0.01 μm (very fine colloidal particles) to 100.0 μm (coarse particles) [36]. However, technology

enhances the incorporation of nanoparticles nowadays. The incorporation of nanofillers instead of microfillers should favor phenomena associated with atomic and molecular interactions that would lead to new macroscopic properties for organic coatings. One of the most studied nanoparticles is TiO$_2$ [47,48]. TiO$_2$ has two different crystal structures: rutile and anatase. The latter one has deformed ions in the crystal lattice of its surface. These ions are easily reduced to a lower oxide state by ultraviolet light releasing highly reactive nascent oxygen, which rapidly oxidizes the surrounding resin to form water-soluble breakdown products. While the reduction reaction at the pigment surface is reversible, the oxidation of the resin is not. This degradation of the resin is manifested as a severe chalking. While generally considered a disadvantage, the aggressive chalking tendency of this pigment has been used in certain self-cleaning house paints [49]. Rutile titanium dioxide, unlike anatase, has a more compact lattice structure with less deformation, and the oxygen is less readily abstracted [34].

The incorporation of pigments to the resin modified an important number of coating characteristics, such as film formation, mechanical properties, certain thermal properties, water permeability, stress development, physical aging, and glass transition temperature [41]. These modifications depend on the PVC defined as [41,50]:

$$PVC = \frac{Vp}{Vp - Vr} \times 100$$

Where Vp is the total pigment volume and Vr is the resin volume.

An important concept is the critical pigment volume concentration (CPVC) [50]. The CPVC is defined as "the point where there is just enough binder to fill in the voids and wet the pigment particles" [51]. Below the CPVC, the coating film is continuous and made only of binder and pigments. Above the CPVC, the film is discontinuous because of the presence of air pockets (that replace the binder) around pigment particles, and the dry paint film becomes porous [51,52]. In the case of wall and ceiling paints, they are formulated with PVC values near those of CPVC because of the properties and functions the paint will have on service: porous, with high hiding power [40,53]. Changes in porosity, mechanical, or optical properties are employed to determine CPVC in latex paints [54,55].

Coating additives are any substances added in small quantities to a coating to improve or to modify certain properties of the coating material during manufacture, storage, transport, and application of the finished coating [3,56]. Additives may also modify the properties of the three main

components of the paint binder, pigments, and solvent, significantly. Additives are classified as follows:

✔ **Thickening agents**: influence the rheological properties of the paint [13,57].

✔ **Surface–active agents or surfactants**: increase spreading or wetting properties [58,59].

✔ **Surface modifiers**: aid the resin to control surface properties such as gloss [60].

✔ **Leveling agents**: help the wet coating to flow out to a smooth dry film after application and to remove or diminish any surface irregularities such as brush marks, orange peel, craters [60].

✔ **Coalescing agents:** aid in film formation via temporary plasticization of the vehicle [58].

✔ **Catalytically active additives**: include driers and catalysts that accelerate the chemical reaction that will conduct to dry coating [61,62].

✔ **Antiskinning agents**: slow down the action of the driers, to avoid the curing of the coating during storage and transportation [63,64].

✔ **Special effect components**: the remaining additives with the ability to integrate some extra property to the paint are included in this group, e.g., light stabilizers (resistance to UV), flame retardants (to prevent the combustion process), corrosion inhibitors (for anticorrosive paints), and biocides (to protect liquid and solid paints from microbiological deterioration).

Therefore, functional coatings integrate one or more components in their composition that impart some special property sought; among the most economically important are corrosion inhibitors and biocides.

Biocides are added to formulations to avoid biodeterioration of paints. Generally in a concentration below 5%wt, they are considered as additives [1]. There are biocides that result to be functional in dry films (in-film) while others seek it in the liquid product (in-can). In the last decades, the concern about the environmental impact of biocides has led to new legislations with restrictions on the use of compounds such as aromatic and halogenated derivatives while others are no longer allowed, as is the case of phenylmercurials [65]. Nowadays, due to different regulatory requirements and to achieve a broader range of activity, the trend in most countries is to combine active ingredients to obtain more effective ("booster") biocide compositions to formulations [66].

The general requirements for in-film and in-can biocides are similar: broad spectrum of activity; cost effectiveness; stable under pH conditions; compatible with the other components; long-lasting activity; and eco-friendly and regulatory compliance. But some of the specific requirements are different with regard to biocides functional in-film: water solubility, leachability, and volatility have to be low, while high partition coefficient between organic materials and water is required, which is the opposite in the case of in-can [66,67].

The most used biocides in coatings can be classified according to their mechanisms of activity which can be summarized as follows [66–68]:

✔ Electrophiles: react with nucleophilic functional groups from bio-molecules, in particular enzymes in microbial cells. Some of the most commercially used ones are formaldehydes, formaldehyde releasers, isothiazolinones, carbamates, and metallic salts of silver and copper.

✔ Membrane-active: react with cell membranes leading to its disruption. Among these are counted alcohols and phenols derivatives and quaternary ammonium salts too.

Besides some bioactive pigments, zinc oxide or barium metaborate may also be included in formulations [67].

Mostly when it mentions *antimicrobial or hygienic coatings*, these refer to a wider spectrum of functionality because of the fact that they are designed to prevent both bacterial and fungal infections especially in medical and institutional sectors, food industry, and similar areas [67,69]. Therefore, functional antimicrobial coatings must include in their formulations one or more anti-bacterial active ingredients to achieve this goal. A conventional compound usually added is triclosan (5-chloro-2-(2,4-dichlorophenoxy) phenol).

The field of antimicrobial coatings study is very active in the present. New eco-friendly materials to replace some questioned biocides by their toxicity with similar or superior efficiency need to be developed. Among the compounds intensely studied are nanoparticles, quaternary ammonium salts, natural products, and derivatives [70–72]. Other strategies seek to modify the surface characteristics to avoid the adhesions of the cells to the surfaces by the reduction of surface energy (easy to clean) or introduction of photocatalytic or superhydrophobic properties (self-cleaning) [4,73,74].

2.1 Biodeterioration of waterborne paint

Service life of coating systems is weathered by environmental factors (thermal changes, water, UV, chemical pollutants, and organisms) that will depend on their location. Among biotic factors, there are microorganisms

that find in paints a substrate where they can grow producing discoloration, chemical degradation, cracking, and finally delamination, therefore shortening their service life [75,76]. On the other hand, more evidence has recognized microbial contamination of surfaces in indoor environments as frequent source of infections [77–79]. The mixture of microorganisms (viable and nonviable), fragments thereof, toxins, allergens, volatile organic compounds, and other chemicals, generated from established biofilms, are harmful for health of people who live or work in dwellings and buildings [12].

Paints are target of microorganisms especially waterborne ones because of the organic components in their composition and the use of water as solvent [10,67]. Outdoor fungi, cyanobacteria, and algae cause defacement of painted structures especially in the tropics, but a larger range of micro-organisms are found in indoor coatings with the predominance of fungi and actinomycetes [75,80]. It could be said that fungi have long been considered the major deteriogens of painted surfaces, especially those which produce dark–pigmented spores such as species of *Aureobasidium*, *Cladosporium*, *Alternaria,* and *Chaetomium* [80,81]. After spore irreversible adhesion and germination, filamentous fungi develop a characteristic apical growth through hyphae that creates a complex network (mycelium) [82]. Added to the invasive growth, they release a great amount of acids and enzymes to their environment to degrade it, which ends in the break of protective coatings [75]. The consequences of this can be observed in Fig. 7.3 where a waterborne paint film inoculated with *Alternaria alternata* and incubated
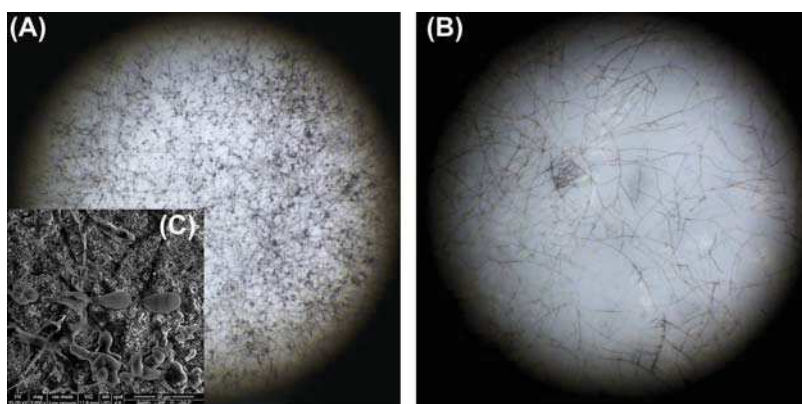

Figure 7.3 (A) Waterborne acrylic paint film inoculated with *Alternaria alternata* and incubated at 28°C for 4 weeks; (B) reverse of the same sample, which allows to observe the complex hyphae network that penetrates the thickness of the coating (images obtained with a binocular microscope); (C) SEM micrograph: active growth of *A. alternata* on the paint film.

at 28°C for 4 weeks is shown (images were obtained with a binocular microscope). Fig. 7.3A shows the inoculated surface and Fig. 7.3B the reverse of the sample applied on glass which allows observing the fungus hyphae that penetrates the thickness of the coating.

Biodeterioration of coating systems depends on many factors; however, the amount of bioavailable water in the material is the most important one [10,83]. Fungi that colonize and grow on building materials have been grouped by Grant et al. [10], taking into account their water requirements on substrates as *primary colonizers*, capable of growth below a water activity (aw) 0.8, among which are included species of *Aspergillus*, *Penicillium*, *Wallemia*, and *Eurotium*; *secondary colonizers*, with a minimal aw between 0.8 and 0.9 are species of *Cladosporium*, *Phoma*, *Ulocladium*, and *Alternaria*; *tertiary colonizers*, demanding at least an aw of 0.9 including species of *Stachybotrys*, *Chaetomium*, *Trichoderma*, and *Aureobasidium* [10,83,84]. In buildings, bathrooms are an extreme example where humidity and temperature cannot be constant and fungal species such as *Alternaria*, *Cladosporium*, *Phoma*, and *Aureobasidium* easily reattain growth from the hyphal tip within 60 min, whereas other fungi such as *Penicillium*, *Fusarium*, *Verticillium*, and *Trichoderma* need 1–2 days [83]. The worst scenario for homeowners is produced by consecutive episodes of water damage that promote fungal growth and mycotoxin synthesis, followed by drier conditions that facilitate the liberation of spores and hyphal fragments [84].

Many raw ingredients of paints provide nutrients for microorganisms. Resins and additives that have large molecular weight must be depolymerized to pass through cellular membranes. Microorganisms excrete substances such as organic acids and enzymes that allow them to hydrolyze certain polymers. Resins with ester bonds like some polyurethanes have been found to be more susceptible to microbial attack and experience more in-service failure than those based on polyether because of the susceptibility of the ester to a large number of microbial enzymes (the hydrolases) [75]. In the case of additives conformed by small molecules, they are most easily affected, and although they are in lower concentration, their degradation can cause important losses in the functionalities of the coating systems and therefore affect their performance [65].

Organic acids released by fungi such as oxalic, oxalacetic, citric, gluconic, oxoacetic, and fumaric form complexes with ions of calcium, aluminum, iron, manganese, silicon, and magnesium contribute to the degradation of materials [85,86]. This was studied by Gu et al. [87] who determined weight loss and the release of calcium from concrete samples exposed to the growth of *Fusarium* isolates. Fungal organic acids are
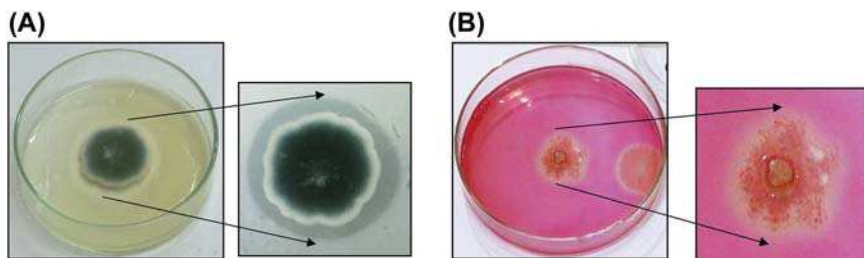
Figure 7.4 (A) Acid release test against *Penicillium* sp.; in detail, halo of degradation can be seen around the fungus (culture medium supplemented with calcium carbonate); (B) cellulolytic activity test against *Chaetomium globosum* evidenced with Congo red dye (culture medium supplemented with cellulose). Both fungi were isolated from biodeteriorated paint films.

evidenced in in vitro tests by supplemented culture medium with calcium carbonate. In Fig. 7.4A, a halo around *Penicillium* sp. colony due to the reaction of calcium carbonate with the organic acids released by the fungus can be observed (isolated from a biodeteriorated coating) [88]. Waterborne paints usually have calcium carbonate in their composition as extender pigment and the quality of the paint is often directly related to titanium dioxide/calcium carbonate ratio [67]. Therefore, low-quality paints would be more susceptible to fungal spoilage.

Cellulose-based thickeners (e.g., carboxymethyl–, hydroxyethyl–, and methyl cellulose) are target to enzymes released by microorganisms. Cellulose is usually broken down to glucose through an enzyme system known as cellulase complex. The reduction in the degree of polymerization of these thickeners results in the loss of paint viscosity during storage [89,90]. Microorganisms' cellulolytic activity can be assessed in an in vitro test based on the formation of clear zone around the colony growing in a culture medium supplemented with cellulose and evidenced with the use of congo red dye [91]. In Fig. 7.4B, cellulolytic activity test can be seen against *Chaetomium globosum,* an ascomycetous commonly encountered in products or cellulose-containing materials in moldy buildings [81].

2.2 Waterborne functional paints: advance in antimicrobial formulations

2.2.1 Inorganic and organic compounds with antimicrobial potentialities to coatings

The search and study of alternative antimicrobial ingredients to replace commercial ones has led to the production of a large number of published works on the subject. Fewer publications are found in relation to the

specific application of these in efficient waterborne paint formulations. In relation to articles that deal specifically with this topic, it can be observed that there is diversity in assessment methods (e.g., agar diffusion, immersion in cultured medium, standard ASTM D5590, standard BS 3900, standard JIS Z 280, standard PN-EN ISO 846, and standard GB15979) and microorganisms selected as target. Mostly, the tests performed are carried out in controlled laboratory conditions and, therefore, more field tests are needed.

Some of these technological advances that stand out in the field of biocides and coatings technology will be further mentioned.

Among the most intensively studied materials, in the last two decades, are those on the nanoscale. This is reflected in more than 1800 products that have been inventoried for the Woodrow Wilson International Center for Scholars through Nanotechnology Consumer Products Inventory project [92]. This explosive growth is directly related to the increasing availability of methods of synthesis and characterization. The improvement of techniques such as scanning electron microscopy, spectroscopy, and crystallography has allowed deepen knowledge of the nanostructures. Therefore, it has been verified that, for the same chemical composition, physical and chemical properties of nanostructures are different from those of a single atom (molecule) and bulk matter; in this sense an essential issue is the size effects [93]. A nanomaterial can be defined as a solid phase where at least one dimension is in the nanometer range $1-100$ nm [93]. They have a higher surface/volume ratio than bulk ones, and it should be considered that the majority of the atoms are located on their surfaces [6,95]. This fact has a huge effect on the properties of dispersed systems as paints contain nanoparticles. For example, a typical pigment as TiO_2 used in paint formulations with a particle size of 300 nm has a specific surface area of 5 m^2/g, while the same component with a size of 21 nm has a specific surface area 10 times higher [94]. This means that comparatively for a same concentration in volume, a considerable improvement of the properties can already be achieved, which allows decreasing the volume contents of the respective components.

The bioactive properties of different nanoscale materials have been studied and the metallic ones have been proved to be active, especially Ag, Cu, Se, and Au [74,96]. Smaller particles increase the probability of contact with microorganisms and increase biocidal efficiency. Assessment of their antimicrobial properties is particularly timely if it is taken into account the concern for the increase of new resistant strains of bacteria to potent

antibiotics [95]. Nanoparticles of TiO_2 and ZnO are also being studied for their photocatalytic activity, which is useful to integrate the self-cleaning function to coatings, especially for exterior applications [74,97].

A promising field is the nanoparticles synthesis by green methods that use microorganisms and aqueous plant extracts (especially these last ones due to being accessible, effective, safe, inexpensive, and eco-friendly) [98]. These methods offer vast possibilities considering the great diversity of organisms with a wide range of metabolites which can serve as reducing and stabilizing agents [99]. The use of natural products in the synthesis process may contribute with other active ingredients that are part of the organism metabolism and therefore can contribute with a synergistic effect on the activity of the nanomaterial. It can be mentioned as alkaloids, polyphenols, terpenes, and peptides, among other components [100,101].

There is an increasing interest in the study of silver nanoparticles especially those obtained by green synthesis because of their wide range of antimicrobial activity and the large number of potential applications in human health, coatings, fabrics, surface treatment, etc. [98,102]. In a previous published work, Ag, Cu, and ZnO nanoparticles were directly added in a waterborne acrylic formulation in different concentrations to assess their efficiency in a 4-week bioresistance test in plates which showed that the best results were obtained with the paint with Ag nanoparticles with the smaller size [103]. Similar results were obtained with the incorporation of Ag nanoparticles synthesized using aqueous plant extract of *Laurelia sempervirens* (laurel) [102]. However, later studies showed that natural aging of these coatings led to a decrease in antifungal efficiency, and because of this, a new approach was needed [104]. Silver nanoparticles are very chemically reactive and possibly would be oxidized at the contact with other components of the formulation like TiO_2 [105]. This loss of paint efficiency can be addressed through the use of solids or matrix that supports the particles to extend their functionality once the coating system is integrated. These solids could be pigments (e.g., TiO_2 and $CaCO_3$) or siliceous–based materials: artificial (e.g., sol–gel) or natural (e.g., clays and zeolites); some of them have been historically used as pigment or fillers in paint formulations [104,106−108]. Over this topic we will return later in this chapter.

On the other hand, in relation to the advances in organic compounds with antimicrobial activity, natural products are an interesting subject. This kind of research is based on the fact that biomolecules from defense system developed by plants and animals against pathogens could be applied to

functionalized coatings [41,47]. Natural metabolites such as peptides, terpenic compounds, polyphenolic, and enzymes have been assessed with these technological purposes [47−49].

Antimicrobial peptides have been intensely studied in the past 20 years, and over 1500 from microorganisms, insects, amphibians, plants, and mammals have been described [109]. Immobilization of these peptides in polymeric matrix to obtain antimicrobial surfaces through thin coatings has been assessed mostly against bacterial strains [70,110].

Products obtained from plants stand out like polyphenolic and terpenic compounds. In the case of polyphenolic compounds, this has been applied mostly in antifouling and anticorrosive paint formulations with promising results [111,112]. Essential oils are widely studied because of their antibacterial and antifungal activity to be applied to surface treatments by thin layers; some examples of this are those obtained from anise, garlic, cinnamon, oregano, and clove essential oils [113−116]. Among derivatives from plant oils used on coatings technology, it could be mentioned eugenol, thymol, carvacrol, and Manuka oil [117,118]. It is interesting to mention the efforts in the development of new formulations of bioactive polyurethane-based coatings that use vegetable oils like urushiol from *Toxicodendron vernicifluum* (lacquer tree) and polyol from *Linum usitatissimum* (linseed) [119,120]. Take into account that conventional polyurethanes are usually synthesized with polyols derived from petroleum, which consume much energy and result in big environmental pollution [121].

In regard to the use of natural products, this results advantageous for coming from renewable resources and be environmentally friendly, but on the other hand, some of them, especially essential oils and derivatives, because of being volatile, tend to escape from the system, and therefore its antimicrobial functionality decreases. In this sense, some strategies are being developed and will be mentioned below.

2.2.2 Modified paint components to improve functional antimicrobial performance

The development of new functional (more efficient and eco-friendly) coatings without disproportionately increasing costs is the goal of several research groups throughout the world. Some strategies to achieve these goals take into account the way in which a biocide is added to a formulation, and a summarized scheme is showed in Fig. 7.5. The usual practice of addition of biocides in coatings is directly its dispersion when the paint is being elaborated, but as it was mentioned before, this approach is not often
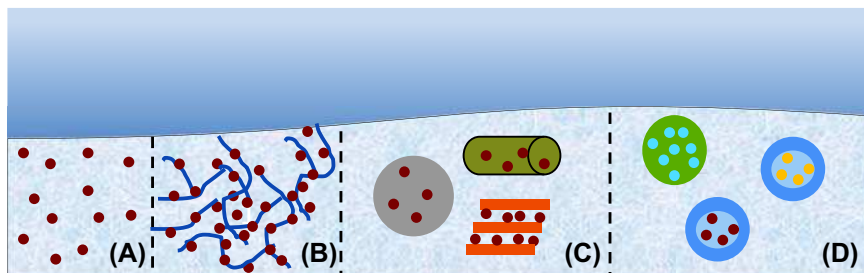
Figure 7.5 Biocide can be introduced into a paint formulation: free (A); associated to paint components: polymers/resins (B); pigments/fillers (C); and encapsulated (D).

satisfactory due to the fact that the biocidal activity is over long before the desired life time of the coating. Usually coatings in the built environment exhibit biocidal functionality less than 2 years in extreme conditions, whereas the desired service life would be at least 10 years [122]. Some possible causes that could be mentioned are as follows:

- ✘ Loss of bioavailability of the antimicrobial ingredients due to be engaged in interactions or reactions with resin, pigment, and other additives [66].
- ✘ Low retention or degradation of the bioactive component in the coating system [106,123].
- ✘ Incompatibility between different biocides within the paint [124].

For a better approach to solve these issues, the architecture of the paint films must be considered. Generally, waterborne paints contain aqueous dispersion of polymer lattices, which after drying leads to the emergence of macroscopic pores unlike what happens with solvent-borne ones, where the resin is dissolved in the solvent. Therefore, this type of porosity would favor the release of the active additives which reside in the pores or area-dsorbed on the surface particles [124]. Some of the strategies currently developed seek to associate the antimicrobial ingredient in an organic or inorganic matrix by electrostatic or covalent bonds to control their release from films [123,125]. Modified paint components used are resins, pigments, and fillers (Fig. 7.5B and C) to retain active substances for longer, avoid degradation, and maintain the bioavailability in the coating systems [104,106,107]. It should be noted that the use of extender pigments or fillers is highly convenient because of being a low-cost alternative. There are published data pointing in the direction that it has been achieved to integrate compounds such as nanoparticles, peptides, quaternary ammonium groups, or conventional biocides to some paint component [72,106,122,123,126].

Among the pigments most usually used to incorporate antimicrobial actives is TiO_2 which has been associated or "decorated" with Ag nanoparticles to be used in waterborne paints by Dominguez-Wong et al. [126]. The antibacterial biofilm activity of the coating was assessed at different humidity conditions in laboratory trials, finding that at lower relative humidity, the antibacterial activity dropped significantly [126].

Particles of $CaCO_3$ were subject of modifications to gain bioactivity by self-assembly technique [127]. In this sense, the 3 μm particles were covered by polystyrene polymer functionalized with an ammonium quaternary salt and showed to be active reducing the number of viable cells of a biofilm significantly [127].

The use of siliceous matrix as framework to include conventional biocides to waterborne paints, firstly, reported by Edge et al. [123], proved to have a longer effective activity because of being protected from the environmental degradation [123]. It is worth noting the work carried out by Arreche et al. [104] who use siliceous matrix obtained by sol–gel method as framework to include Ag in an indoor waterborne acrylic formulation. The paint with Ag-silane showed good results even after being subjected to natural aging (exposed to sun light through a window glass) in laboratory conditions for a period of 6 months [104].

Other attempts were made strictly on paint technology application but using other siliceous matrix has been reported. In this sense, the use of modified natural clay such as halloysite nanotubes loaded with carvacrol (essential thyme oil derivative) to formulate waterborne polyurethane coatings with antibiofilm activity is highlighted [106]. Clay minerals (e.g., montmorillonites and halloysite) have the ability to exchange ions and be modified to a nanoscale level to work out as carriers for inorganic and organic compounds [128,129]. Another aluminosilicate intensively studied are zeolites that can be modified to gain functionality through ion exchange [130]. There are some articles that present modified zeolites exchanged with La^{3+}, Ag^+, and Zn^{2+} among others to be used in paint formulations [108,130]. Zeolites with Ag^+ and Zn^{2+} probed to be efficient against fungi when incorporated in a waterborne acrylic formulation [108].

Taken into account, natural silica-based material to be used as frameworks or supporting structures, diatomaceous earths result a highly promising alternative. This filler is an unconsolidated sediment constituted from an accumulation in oceans or freshwaters of dead diatoms (microscopic single-cell algae), which has the advantage of being abundant and

cheap as resource [107,131]. Several methodologies can be used to modify and activate the diatomite surface [131,132]. It has been recently reported by M. Fernandez and N. Bellotti [107] the modification of diatomaceous earths to be associated with quaternary ammonium groups with future coating technology applications showed satisfactory antifungal and antibacterial activity.

Another more sophisticated and therefore costly possibility is the inclusion of biocides in micro- and nanocapsules and spheres (Fig. 7.5D), which can solve, among other things, the issue of compatibility between biocides [124,133]. Micro- and nanocapsules refer strictly to those products designed to be integrated into the paint as capsules with spherical shape constituted by a polymeric shell with the required biocide inside them. In this sense, micro- and nanocapsules made by polyethyleneimines with sodium benzoate as active ingredient [133] and poly(lactic acid) with conventional biocides [134] have been reported.

On the other hand, micro- and nanospheres defined as homogeneous spherical particles where the biocide is dissolved or dispersed (not necessarily uniformly) in a polymer matrix were reported [135]. Some examples are microspheres base on poly(methyl methacrylate) in which medetomidine was dispersed and then added to a water-based standard exterior wall paint that proved the slower release of the biocide [135,136]; in the case of nanospheres, sol−gel method has been performed with Ag and Cu nanoparticles, which then were incorporated to architectural paints and assessed in controlled conditions and those that contained Cu showed a broader spectrum of antimicrobial activity than those with Ag [136].

Other field of research involves the use of modified polymers. In this sense, acrylic resin has been associated with ZnO nanoparticle and the system obtained proved to have both antielectrostatic and antibacterial functionalities with a concentration ∼5 wt.% in controlled conditions [137]. Also, polymeric N−halamine latex emulsions were developed with the goal to obtain an antimicrobial paint with a broader biocidal efficacy; from laboratory trials, the paint films successfully prevented bacteria biofilm formation and completely inhibited fungi and virus growth [138]. Polyurethane has also been used to obtain an aqueous polymer system with good antibacterial properties. In this case, the polymer was designed and synthesized employing an L−lysine-derivatized diamine containing a quaternary ammonium salt, which showed antibacterial activity [139]. But further studies need to be performed to obtain an efficient antimicrobial functional paint with this bioactive resin.

Acknowledgments

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