

Biodegradation of paints: a current status

H.R. Ravikumar¹, Shwetha S. Rao² and C.S. Karigar^{2*}

¹Department of Biochemistry, Rayalaseema University, Kurnool- 518002, India

²Department of Biochemistry, Central College Campus, Bangalore University, Bangalore- 560001, India
ravi333ivar@gmail.com¹, shwethashamarao@gmail.com², karigar@bub.ernet.in^{2*}

Abstract

Paint and painting has been practiced since ancient times. Several paints of varying chemistry have been in use for domestic and industrial purposes. The painted surfaces undergo damage or discolored due to natural weathering, and the growth and activity of living organisms. The knowledge of paints and their composition is essential to understand their fate in the natural environmental settings. Microorganisms participate in the mineralization of paints through biofilm formations on the surfaces like stone buildings causing aesthetic and structural damage. Various types of organisms are involved in paint spoilage and they include bacteria, fungi, algae, and protozoa. The interactions between these organisms can enhance or retard the overall rate of paint biodegradation. In this review a brief description of the paints and their compositions, paint properties, paint biodeterioration and biodegradation are described.

Keywords: Paints, composition, biodeterioration, biofilms, bacteria, fungi, algae

Introduction

Paint is one of the oldest synthetic substances known to mankind, with a history stretching back into pre-historic times. During prehistoric times clays and chalks were mixed with animal fats and used as paints to depict hunts on the cave walls. By 2500BC the Egyptians had improved the paint manufacturing technology and developed a clear blue pigment by grinding azurite, gums, wax and albumen (egg white). Further, the paint technology was improved during the first millennium BC as the Greeks learnt to blend paints with hot wax, rather than water, making a paint that was both thicker and easier to spread and thus making it possible to blend colours. By this time many colours were available from both natural and synthetic sources, one of them being a purple pigment made from heating yellow earth until it turned red and then plunging it into vinegar. The technology then lapsed for many years, with techniques being passed down from generation to generation by travelling craftsmen. This continued until the eighteenth century, when paint factories began to be opened in Europe and America, and by the nineteenth century due to mass production the houses began to be painted. Now, the chemistry of paint manufacture and function are understood, such that paint manufacture has finally moved from being an art to being a science.

Types of paints

Modern household paints fall into two broad categories: a) Orthodox, oil-based paints, thinned with mineral turpentine or other organic solvents and b) Emulsion paints, which may be vinyl or acrylic based and which are thinned with Water (Clark, 1983).

The composition of paints

Paint is essentially a mixture of i) binder, which adheres the paint to the surface, ii) pigments, which give the paint a colour, opacity and occasionally prevent

corrosion, and iii) solvents to make the paint spreadable. The chemistry of these components is outlined below.

Binders

The binder is required to hold the pigment adhered to the surface. The binder is usually a polymeric substance, and is either dissolved in the paint or suspended in it by using emulsifiers. Paint technology has advanced very little until this century. Even as recently as the 1960s the 'drying oils' were the most common paint binders. Drying oils are substances that, when spread out as a film, will dry to form a continuous skin. Linseed oil, the most common example of a drying oil, will dry in 2 to 3 days while other oils, such as soya bean oil, may take up to 10 days (Clark, 1983). Linseed oil is a mixture of triglycerides of long chain carboxylic acids. Some of the major component carboxylic acids are: linolenic acid, linoleic acid, oleic acid, palmitic acid and stearic acid. Many common drying oils contain these compounds and also include eleosteric and ricinoleic acids, in various ratios. The drying process is a complex one of polymerization, probably catalyzed by peroxides. Composition of the natural compounds varies widely and the proportions of the constituent triglycerides will vary from batch to batch of oil. Various processes have been used to improve the properties of oils; one among them is the increase in the molecular weight of the oil by controlled oxidation.

Driers

Driers are used to develop a rapidly drying skin on paint by oxidation. The benefits are to develop touch hardness sooner, and avoiding problems associated with insects crawling on wet paint surfaces, or water splash. Driers are a group of metallic soaps or salts containing either alkaline-earth metals or heavy metals. They are added to air-drying coating systems to catalyze the oxidative cross-linking reactions (Oyman, 2005). Driers

are divided into two classes as those that affect the oxidation of oils (primary) and those that affect the polymerization process itself (secondary). The oxidative driers can be surface driers (cobalt, manganese, vanadium) or through driers (lead). The polymerizing driers are often metals with only one possible oxidation state (zinc, calcium, potassium, lithium, sodium) (Tumosa & Mecklenburg, 2005). The drying process of paint is accelerated by the addition of small quantities of organometallic compounds. These compounds accelerate film formation and have the highest catalytic activity. Lead compounds are rarely used in modern paints due to their high toxicity. The organometallic compounds results in the rapid setting of film surface to a near solid while the underlying film does not even reach the advanced state of oxidation. This uneven hardening in thick films will cause the defect known as wrinkling (www.howeverythingworks.org & www.epa.gov).

Alkyd resins

The most important and extensively used solvent-based resins in the paint industry in recent years are the alkyd resins. In the process of etherification reaction the large resin molecules of alkyd resins are built up, hence they are classified as polyesters (Clark, 1983). An ester is produced by heating an alcohol and acid together. Esters formed in this type of reaction from mono functional constituents are chemicals of fixed, known and easily determined molecular mass and structure. In presence of poly functional ingredients more complicated reactions will occur. This type of reaction is carried out in an inert gas blanket at temperature of 180-250°C, in the presence required acid value or, alternatively, the required viscosity. The commonest starting products for the class of alkyd resins are glycerol and phthalic anhydride. Other common components of alkyd resins are acids and alcohols but alone are of little practical use in the manufacture of paints. Films formed from them yield dull, soft, tacky films of poor durability. By incorporating oils in the reaction mixture some of the long chain carboxylic acids in the triglyceride are replaced by difunctional acids. This incorporation provides resins that yield films with good durability, excellent colour retention and superior gloss to films formed from drying oils alone. These are known as oil modified alkyd resins. Many agents have been used to modify the alkyds for use as paints (Table 1). Many modern "oil-based" paints are alkyds modified in

Table 1. Additives used in alkyd resins

Additive	Function
Styrene	Reduce drying time, Improve durability of paint
Methyl styrene	Reduce drying time, Improve durability of paint
Methyl silane	Co-polymerise to make more durable glossy paints Especially effective with dark paints
Abietic acid	Dries quickly, Produces glossy paints, Soluble in aliphatic solvents
Bisphenol A	Resistant to water, alkali, grease and oil Hard surface, Glossy finish

some way or other. Alkyds are used in both air dry paints and heat cured "stoving enamels" (Huber & Stoye, 2006). A typical alkyd resin for use in glossy household paint would contain the following: glycerol: phthalic anhydride: linseed oil: abietic acid: phenolic resins (135:150:135:35:85 v/v).

Emulsions

Emulsion paint, consists of pigment and solid or semi-solid polymeric particles dispersed in a continuous aqueous medium in which they are insoluble. This emulsion is made from monomers, initiators, water and emulsifiers. Water-based paints based on acrylic and or vinyl emulsions are the most extensively used paints in the retail decorative market (Clark 1983).

The monomers substances which are having its application in emulsion paints include styrene, vinyl acetate, methyl acrylate, butyl acrylate, acrylonitrile, etc. They undergo polymerization resulting in the formation of products often termed as 'acrylics'. The polymerization of the monomers is generally caused by the initiators like per-sulphates. A formulated blend of these monomers is polymerized in water under controlled temperature conditions as the reactions are exothermic. Initiators such as ammonium per-sulphate are added to start the free-radical polymerization. Activators such as ferrous ammonium sulphate are also added to speed up the dissociation of the initiators and hence increase the concentration of radicals. Emulsifiers or surfactants are added to stabilize the emulsion. The final product consists of a suspension of polymer micelles whose diameter is between 0.1 and 1.0µm. Each micelle is coated by a layer of emulsifier, one end of which is attached to the particle while the other extends into the surrounding water, thereby holding the micelle in a stable suspension.

Epoxy resins

Epoxy resins were first derived from bisphenol A and epichlorohydrin (IARC 1989), and introduced into the paint industry in the late 1940s. Two major types of epoxy resin exist - glycidyl ether epoxy resins and epoxidized olefins, the former being the most common. Epoxy resins based on bisphenol A and epichlorohydrin are the most prominent of the glycidyl ether category. They are produced by a condensation reaction in which bisphenol A and epichlorohydrin are reacted in the presence of alkali. The resultant diglycidyl ether resin has a functionality of two reactive epoxy groups per molecule. Epoxy resins can be polymerized through their reactive epoxy group using acids, amines or polyamides (Brock *et al.*, 2000).

Polyurethanes

These have been developed from a reaction discovered by O. Bayer in Germany in the 1930s. Bayer A. G. is the world leaders amongst the manufacturers of resins used in polyurethane paints. Urethanes are derived by the addition of H-O over the N=C of an isocyanate group. Polyurethanes are derivatives of

urethane which are produced from reaction of difunctional alcohols with difunctional isocyanate. They may be used in the manufacture of foamed plastics, elastomers and surface coatings and paints. Polyurethane paint systems are tough, possess durable films which retain their gloss for long periods and also very resistant to weathering. They are often very easy to clean. Polyurethanes are commonly used for painting aircraft and automobiles. There are many other synthetic resins which are used in the manufacture of paints and these include phenol-formaldehydes, urea-formaldehydes, melamines, vinyls, acrylic resins and chlorinated rubber (http://EzineArticles.com/waheed_hassan).

Pigments

Table 2. Some common classes of organic pigments

Group	Example	Colour*						
		1	2	3	4	5	6	7
Azo dyes								
Monoazo	Arylamide yellow (PY 73)	√	√	√	√	√		
Diazo	Diarylide yellows	√	√	√	√		√	
Azo salt	Barium red 2B toner (PR 48.1)	√	√	√	√			
Azo metal complex	Nickel azo Yellow (PG10)	√		√				√
Polycyclic pigments								
Phthalocyanide	copper phthalocyanine						√	√
Antraquinone	dibrom anthanthrone	√	√	√	√	√	√	√
Quin-acridone	quinacridone red (PV 19)	√		√		√		
Dioxazine	Dioxane Violet PV23					√		
Thioindigo	Tetrachloro thiondigo (PR 88)					√		
*Colour Code 1 = yellow; 2 = orange; 3 = red; 4 = brown; 5 = violet; 6 = blue; 7 = green								

Pigments serve three main functions: the optical function of providing colour, opacity and gloss; a protective function with regards to the surface underneath the paint and with regards to the binder which can be destroyed by UV; and a reinforcing function for the paint itself in that they help the binder to stick. Pigments are composed of tiny solid particles less than 1µm in diameter, a size that enables them to refract light. The pigment to be effective it has to be evenly dispersed throughout the solvent and in contact with the solvent. Surrounding pigment particles is a layer of moist air and, in some cases, other gases. To bring the pigment into contact with the solvent this layer has to be displaced and this displacement is known as wetting. If a pigment is not properly wetted in a paint it may result in colour streakiness in the finished paints, thus solvents and pigments must be chosen that result in a well wetted pigment. Wetting and dispersing agents are used to

improve the wetting properties of the resin/solvent system.

Table 3. Some common inorganic pigments

Pigment	Colour(s)
Carbon black	black
Titanium dioxide	white
Iron oxides	yellow, red, brown, black
Zinc chromates	yellow
Azurite	blue
Chromium oxides	green, blue
Cadmium sulphides	greenish yellow to red to bordeaux
Lithopone	white

A variety of natural and synthetic pigments are used in paints, providing a complete spectrum of colours and variety finishing pattern. Pigments are broadly classified as either organic (Table 2) or inorganic (Table 3) (Bentley & Turner 1998; Stoye & Freitag 1998; Brock *et al.*, 2000; Smith 2002). Organic pigments are usually preferable as in general they are: brighter, stronger, more transparent, and more stable. In addition they have greater tinting strength, better gloss development and some absorb UV light, preventing it from damaging the binder. However, inorganic pigments are also widely used as they do not bleed, and are heat and light stable and are much cheaper than organic pigments. In addition they are used for some specialist pigments, and for black and white pigments, as it is not possible to get pure black or white organic pigments. One such white pigment, titanium dioxide, is widely agreed to be the single most important pigment in use today. It is the strongest known pigment in terms of both opacity and tinting power which, coupled with its pure white tint and its fine particle size, means that it can be used as an opacifier to prepare films with a high hiding power and to reduce pigment content. This has resulted in paints with much improved elasticity and hence improved durability. Pigments provide other properties to paints than just colour and hiding power. Anti-corrosive pigments inhibit the corrosion of steel. The anti-corrosive pigment which has been used for many years is red lead (Pb_3O_4). In combination with linseed oil, red lead in the past has been used as the standard anti-corrosive primer for iron and steel. Anti-corrosive pigments for iron and steel commonly in use include zinc phosphate, zinc chromate, zinc molybdate and barium metaborate, although alternatives to chromates are being sought as they are toxic and environmentally hazardous. Addition of mineral compounds to the paint results in the improvement of application characteristics. These are known as 'extenders' and are a very important part of the paint formulator's 'tool kit'. The extenders (Table 4) may be used as "flattening agents" to provide flat or semi-gloss finishes, to prevent settlement of pigments or provide better keying (sticking) properties for subsequent coatings.

The metallic pigment has become important in recent years. Finely divided aluminum plays the major role in the metallic finishing of modern car paints. Bronze may also be used as a decorative pigment. Zinc and lead powders

Table 4. Common extender pigments

Common name	Formula	Uses
Whiting	Calcium carbonate	undercoats and flat paints
Talc	Hydrate magnesium silicate	assists TiO ₂ dispersion, improves sanding
Barytes	Barium sulphate	traffic paints (wear resistant), pigment extender
Kaolin	Hydrated aluminium silicate	assists TiO ₂ dispersion, decreases viscosity
Silica	Silica	flattening agent, traffic paints (wear resistant)
Mica	Hydrous aluminium potassium silicate	chemically and solar resistant, improves water resistance

may also be used as pigments, but in this case the metal powder has anti-corrosive properties. Galvanic-type coatings containing zinc powder are of important tool in the protection of steelwork, and are the subject of continuous research and development.

Solvents

Solvents are necessary to ensure an even mixing of the paint components and to make them easy to apply. The solvents used differ with the way in which the paint will be applied as the drying rate differs on the manner of application, e.g. the solvents in spray paints need to evaporate much more quickly than those in brush-applied paints. In general, a blend of solvents is used to produce a paint that will surface and through dry (i.e. dry throughout) at the correct rate without uneven shrinkage. White spirit and mineral turpentine are probably the most widely used solvent, however many other compounds like toluene, methyl ethyl ketone, methyl isobutyl ketone, xylenes, butyl acetate and methoxy propyl acetate find its application in paint formulation.

Biodeterioration

"Biodeterioration" and "bioremediation" are the two aspects of biodegradation with an anthropomorphic emphasis. Biodeterioration is the breakdown of economically useful substances often the term is used narrowly to refer to the deterioration of substances that are normally resistant to biological attack such as metals, plastics, drugs, cosmetics, paintings, sculpture, wood products, electrical equipment, fuels and oils, and other objects (Sarkar *et al.*, 1997). In bioremediation, biological systems are used to transform and/or degrade toxic compounds or otherwise render them harmless. Bioremediation can involve indigenous microbial populations with or without nutrient supplementation, or it can involve inoculation of exogenous organisms into the site. When exogenous organisms are added, the process is called "bioaugmentation." In either Case, the goal is to disharm noxious chemicals without the formation of new toxins. Micro-organisms have a simple approach to life; they use whatever is available as a food source, attach themselves to practically all surfaces, multiply and build up biomass. Everyone is familiar with the phenomenon of rotting, the natural decay and recycling of materials by a

wide range of life forms, including micro-organisms. This process is termed as biodegradation and it is perceived as a beneficial or positive process. Biodeterioration may be defined as 'the deterioration of materials of economic importance by micro-organisms'; it is perceived as a deleterious or negative process. Biodeterioration has been classified as follows: Mechanical biodeterioration, Chemical assimilatory biodeterioration and soiling.

Mechanical biodeterioration

This occurs when the material is damaged as a direct result of the physical activity of an organism, such as its movement or growth. An example of this kind of biodeterioration is the damage caused to electrical cabling as a result of insect or rodent attack.

Chemical assimilatory biodeterioration

This is perhaps the most common form of biodeterioration. It occurs when a material is degraded for its nutritional value. For example breakdown of cellulosic materials such as wallpaper by cellulolytic fungi is an example.

Chemical dissimilatory biodeterioration

This occurs when a material is damaged as a result of the production and release of metabolic products by microbial activity that may corrode pigment or toxify the material. The poisoning of grain by mycotoxins and the release of pigments into plastic films are examples of this process.

Soiling

This visible form of biodeterioration occurs when the mere presence of an organism or its excrement, renders the product unacceptable. The function of the material may be impaired by the presence of the organisms, as in the fouling of ships' hulls by barnacles and algae. It is essential to appreciate that more than one of these biodeterioration processes, or indeed all of them may be occurring at the same time. Materials of economic importance known to be subjected to biodeterioration include: stored agricultural products, archival material products, pulp paper, wood and allied textiles and leather, constructional materials, fuels and lubricants, pharmaceuticals, metals cosmetics, paints, polymers, rubbers and stone, buildings, glass, adhesives and sealants. The list is extensive and it includes most of the industrial materials that readily come to mind. It is difficult to accept that some of these materials (glass, metal, stone) are susceptible to microbial attack.

Biodeterioration of emulsion paints

Only water-based-paints are susceptible to biodeterioration during their manufacture which may give rise to in-can problems. Thinning of the paint results when the thickener, usually cellulose ether, is attacked by cellulase enzymes produced by bacteria and fungi introduced into the formulation via contaminated components. Talc, which is used as an extender in paint formulation, has been cited as a possible source of contamination. The detection of contaminants at the surface of emulsion paint, together with gas evolution (the

production of 'off odors') have also been attributed to microbial contamination. Films of oil- and water-based paints are colonized by micro-organisms on the outside and inside of buildings (Fig.1). This aspect of biodeterioration can be both unsightly and hazardous to health. (Morton 2001). "Biodegradation" is the biologically mediated breakdown of chemical compounds. It is an umbrella term, encompassing most of the other jargon addressed in this section, and generally implies a series of biochemical reactions. When biodegradation is complete, the process is called "mineralization," i.e., the total breakdown of organic molecules into water, CO₂, and/or other inorganic end products (Alexander 1981).

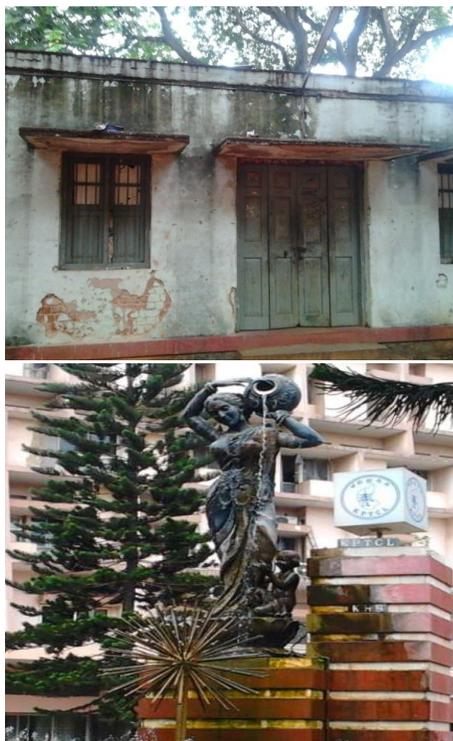
Paint biodegradation

Paint biodegradation is still in the experimental stage. One method among this is to create microorganisms that feed on polyurethane-based paint. This method works, but only very slowly. Another approach is to make paint itself more biodegradable by adding cellulose and elastin. However, that could decrease the life span of paint and require more stripping rather than less.

Biodeterioration of paintings

Paintings are composed of a support (canvas, wood, paper or parchment) a preparation layer and a paint layer, the chemical composition of which varies according to the mode of painting, the kind of paints used (oil paints, distemper or water colour). In canvas paintings, the preparation is usually made with lime or gypsum with addition of animal or vegetal glue. On this smooth surface several layers of colour are present, which consist of pigments mixed with binders of oil or distemper (egg or glue). The surfaces are usually covered with a thin, translucent protective varnish. In paintings on wooden supports, a similar multilayer structure is observed. Paintings on paper can be of water colours, gouaches or pastels. The paint is laid directly on paper and the state of preservation of the paper determines the durability of the whole painting. In water colours, the transparent paint layer also contains a small amount of binder, usually gum arabic. Pastels are made with crayons consisting of pigment without binder and are, therefore, extremely difficult to store and preserve. In painted works of art, the biodeterioration processes can involve either a portion of the painting or all of its components. Thus, paintings may show traces of a biological attack on the reverse side, the support, or on the painted side, and a part or all

Fig.1. Biodeterioration of domestic and public buildings. Biodegradation of paints



components may be damaged. The organic components in paintings represent a good source of nutrition for a wide range of heterotrophic micro organisms. But, biological attack occurs only when there are favorable environmental conditions, and such conditions are often found in museum rooms, old churches or in deposits without any control of the humidity and temperature. The micro-flora attacking paintings include virtually all species of micro-fungi because the variety of organic components of these works of art can represent a carbon source for practically all species. In addition, they show a great tolerance for environmental conditions and can use condensation moisture. In contrast, the moisture content of these objects is rarely so high as to favour development of bacteria, which are unable to use condensation water (Dhawan & Agrawal 1986). Generally, the first part subjected to the microbial deterioration is the support. In fact, in

paintings on canvas, the microbial attack usually starts from the reverse side, because the glue sizing increases the natural susceptibility of textiles. Then the biodeteriogens penetrate inside canvas reaching the back side of the paint layer, causing cracks and detachment, while the cellulose hydrolysis creates differences of adhesion between the paint layer and the canvas itself (Strzelczyk *et al.*, 1987). In paintings on wooden board, the decay of the support can be different from the paint layer. The microorganisms involved in biodeterioration processes are those mentioned for biodeterioration of materials of vegetable and animal origin. Sometimes the presence of substances, such as sizing glue or lining paste used for different treatments of the support, can increase susceptibility (Dhawan & Agrawal 1986; Makies1981). Biological attack on the paint layer is less frequent than on the support and depends on the nature of pigments. The most susceptible to biological attack are casein and egg distemper, emulsion distemper and linseed oil in this order. In contrast, the presence of heavy metals in some pigments, such as lead, zinc or chromium, can increase the resistance of the paint layer for biodegradation. Water colours contain only a small amount of organic binder and are, therefore, as susceptible to microbial deterioration as pastels (Dhawan & Agrawal 1986). The growth of a micro fungal mycelium by a microscopical germinating spora is quite rapid, with radial development, and it become macroscopically visible in few days. Among the species of micro-fungi

Fig.2. Spoilage microorganisms cultured from domestic building surfaces. Paint spoilage microorganisms



Fig.3. Spoilage microorganisms cultured from public building surfaces

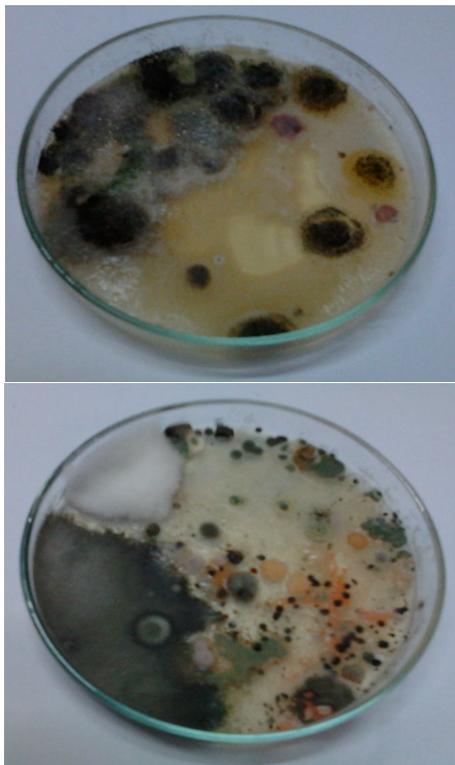


Fig. 4. Microbial activity on domestic buildings



most frequently involved in deterioration of the paint layer, are species of *Penicillium*, *Aspergillus*, *Trichoderma* and *Phoma pigmentovora* which disintegrate distemper and oil binders. *Aureobasidium* decompose oil binders, *Geotrichum* develop on casein binders, *Mucor* and *Rhizopus* attack glue (Gallo *et al.*, 1985). The development of micro-fungi on the surface of paintings induces aesthetical, mechanical and biochemical decay. In fact, the growing mycelium spread over the paints, masking design and colour, while the growth of hyphae and fruiting bodies inside the support can cause friability and loss of the paint layer.

Exoenzyme activities can cause more serious damage by decomposition of some polymers both of the paint layer and of the support, whereas the presence of coloured fruiting bodies and the production of coloured metabolites provokes the formation of permanent stained patches while organic acids produces irreparably modifications in the structure. In biodeterioration of painted materials, insects are also often reported but they only occasionally damage the paint layer, preferentially attacking the wood of the frame or support and the vegetable glue.

Microbial growth on paints and coatings

Paints and coatings are susceptible to bacterial and fungal growth when in the liquid state but prone to colonization, especially by fungi, algae and cyanobacteria after application; components such as residual thickening agents are the most abundant carbon source (Fig.2).

Interior painted surfaces are most frequently colonized by moulds, with yeasts growing in areas with excessive moisture. (Smith 1978) concluded that *Aureobasidium*, *Alternaria*, *Aspergillus*, *Cladosporium* and *Penicillium* were amongst the main contaminants and were able to break down and penetrate the paint film.

The effects of such growth are initially disfigurement of the surface followed by breakdown of the coating and decay or corrosion of the underlying substrate. The growth of photosynthetic organisms is rare on interior surfaces but fungi, Actinomycetes, Cyanobacteria and Algae are all able to colonize exterior painted surfaces (Gaylarde & Gaylarde 2005). Although several groups of workers in the 1960s recognized that algae can produce organic acids which may be corrosive to some coatings, the main effects of algal growth are aesthetic the disfigurement premature redecoration (Fig.3 & 4).

Additionally, the presence of extensive sheets of algal growth will trap water and retard drying which, in turn, will exacerbate water induced damage of the underlying substrate. Further problems may arise from the sequential development of macro-organisms like lichens, bryophytes, pteridophytes and spermatophytes.

General pathway of fungal biodegradation

The fungi secrete extracellular enzymes which break down potential food sources, and absorb nutrients back into the fungal colony. The decomposition of lignocelluloses is probably the single most important degradative event in the Earth's carbon cycle. The

Table 5. Deteriogenic biofilms on buildings

Material	Fungal types	References
Concrete and stone	<i>Alternaria, Aspergillus, Aureobasidium, Botrytis, Candida, Cladosporium, Curvularia, Exophiala, Fusarium, Mucor, Paecilomyces, Penicillium, Phoma, Sporobolomyces, Trichoderma, Verticillium</i>	Gu <i>et al.</i> , 1998; Hirsch <i>et al.</i> , 1995; Leznicka <i>et al.</i> , 1991; Lim <i>et al.</i> , 1989; Line, 1997; May <i>et al.</i> , 1993; McCormack <i>et al.</i> , 1996; Raty <i>et al.</i> , 1994
Metal	<i>Aspergillus, H. resinae, Penicillium, Trichoderma</i>	Salvarezza & Videla, 1986;
Painted surfaces	<i>Alternaria, Aspergillus, Aureobasidium, Cephalosporium, Cladosporium, Curvularia, Exophiala, Fusarium, Geomyces, Mucor, Penicillium, Stachybotrys, Stemphyllium, Trametes, Trichoderma, Ulocladium, Verticillium</i>	Bravery, 1988; O'Neil, 1988; Stranger & Norgaard, 1991;

utilization and transformation of the dead remains of other organisms is also essential to the Earth's economy. An enormous ecological literature is found on the role of fungi as primary and secondary decomposers in nature (Alexander *et al.*, 1981). From the human perspective, the power of fungal enzymes is enormous. Molds destroy more food than any other group of microorganisms. They damage standing timber, finished wood products, fibers, and a wide range of non-cellulosic products such as plastics, fuels, paints, glues, drugs, and other human artifacts (Onions *et al.*, 1981; Rose, 1981).

Table 6. Some bacteria important in the deterioration of building materials

Material	Bacterial groups	References
Concrete, stone and mortars	Sulfur-oxidising bacteria (e.g. <i>Thiobacillus</i>), heterotrophic bacteria (e.g. <i>Arthrobacter, Micrococcus, Pseudomonas</i>), nitrifying bacteria	Cragolino & Tuovinen, 1984; Koestler <i>et al.</i> , 1985; Sorlini <i>et al.</i> , 1994; Tayler & May, 1994; Wales & Sagar, 1985; Wasserbauer <i>et al.</i> , 1988
Metal	SRB, sulfur-oxidising bacteria (e.g. <i>Thiobacillus</i>), iron bacteria (e.g. <i>Gallionella</i>), iron-reducing bacteria (e.g. <i>Vibrio, Shewanella</i>), acid-producing bacteria (e.g. <i>Clostridium</i>)	Cloete & de Bruyn, 1995; Cragolino & Tuovinen, 1984; Gaylarde & Videla, 1987, 1994; Liu <i>et al.</i> , 1997; Walker & Keevil, 1995
Painted surfaces	<i>Actinomyces, Alcaligenes, Bacillus, Flavobacterium, Pseudomonas</i>	O'Neil, 1988

(source: Gaylarde & Morton, 2002)

Paint spoilage by bacteria

In addition to fungi and algae, bacteria are also involved in the biofilm formation followed by reduced durability of structures. While fungal and algal growths are often visible to the naked eye, bacteria can be present on an apparently clean surface in sufficient numbers to exert adverse effects. Such effects can include concrete and metal corrosion due to production of inorganic acids (Cragolino & Tuovinen, 1984; Bock & Sand 1986; May *et al.*, 1993), or blistering of paint due to other microbial metabolic activities (Johannessen & Norgaard, 1991). Chemolithotrophic and oligotrophic bacteria, which grow at very low nutrient levels, may condition a surface, making it more amenable to colonization by other microorganisms (May *et al.*, 1993).

Fungal problems

Discoloration of building materials is often thought to be primarily due to fungi, since they can be highly pigmented and their growth is noticed easily by unaided eye. However algal and bacterial biofilms can also cause superficial red, orange, brown, green and black stains. There has been relatively little work on the deterioration of stone, concrete and cement by fungi, since traditionally the sulfur-oxidizing bacteria have been deemed to be most important (Cragolino & Tuovinen 1984). The production of acids by several filamentous fungi isolated from stone buildings in Brazil has been reported (Resende *et al.*, 1996). McCormack *et al.* (1996) have presented evidence for the acid attack of the fungus *Aspergillus glaucus* on concrete. Gu *et al.* (1998) demonstrated weight loss and calcium release from concrete exposed to a *Fusarium* isolate, and they were also able to demonstrate the penetration of the hyphae into the concrete structure, using SEM. In a review on stone deterioration by fungi, May *et al.* (1993) discussed the involvement of bacteria and, to some extent, algae. Fungi produce a variety of inorganic and organic acids, which can demineralise various stone substrates (Griffin *et al.* 1991). The filamentous form of the microorganisms enables them to penetrate the weakened structure (Koestler *et al.* 1985), especially when extra nutrients, in the form of dirt or algal and bacterial biofilms, are present (Gomez *et al.*, 1994). Fungal growth on plasterboard has been reported to be a significant health risk because of the production of mycotoxins (Raty *et al.*, 1994) and it is well known that sealants used in bathrooms are extremely susceptible to fungal growth. Moriyama *et al.* (1992) isolated 34 different genera of fungi from surfaces in Japanese bathrooms. The activity of fungal biofilms on plastics, particularly polyurethanes, has been investigated by a number of workers (Pathirana & Seal, 1982; Wales & Sagar, 1985; Bentham *et al.* 1988; El-Sayed *et al.*, 1996). Fungal enzymes are able to break down the polyurethanes or metabolize the plasticizers in various polymers (Berk *et al.*, 1957), resulting in embrittlement and loss of strength. This is very significant in polymeric varnishes, where fungal action causes

Table 7. Deteriogenic microorganisms which can affect building materials

Material	Algae	Photosynthetic bacteria	References
Concrete and stone	<i>Apatococcus, Bradeacoccus, Chlamydomonas, Chlorella, Chlorococcum, Chlorokybus, Chlorosarcina, Clorosarcinopsis, Ecdysichlamys, Haematococcus, Friedmannia, Klebsormidium, Leptosiroid, Muriella, Neochloris, Oedogonium, Palmellococcus, Pseudodendroclonium, Scenedesmus, Stichococcus, Stigeoclonium, Tetracystis, Trebouxia, Trentepohlia, Bacillariophyceae, Chrysophyceae, Eustigmatophyceae, Rhodophyceae, Xanthophyceae</i>	<i>Aphanocapsa, Aphanothece, Calothrix, Chaemisiphon, Chroococcus, Gloeocapsa, Hyella, Microcoleus, Myxosarcina, Nostoc, Phormidium, Plectonema, Pleurocapsa, Schizothrix, Scytonema, Synechocystis, Tolypothrix</i>	<i>Danin & Caneva, 1990; Gomez et al., 1994; Grant, 1982; Grant et al., 1989; Ortega-Cal et al., 1991; Rippka et al., 1979; Schlichting, 1975</i>
Metal	Hydrogenase-positive Chlorophyta	<i>Nostoc, Anabaena, purple bacteria</i>	<i>Stanier et al., 1959; Schlichting, 1975</i>
Painted surfaces	<i>Chlorella, Chlorococcum, Eustigmatus, Trebouxia, Trentepohlia, Ulothrix, diatoms</i>	<i>Chroococcus, Gloeocapsa, Gloeothece, Lyngbya, Nostoc, Oscillatoria, Plectonema, Scytonema, Synechococcus, Synechocystis</i>	<i>Gaylarde & Gaylarde, 1998b; Grant, 1982; Grant et al., 1989; Joshi & Mukundan, 1997; Jozsa et al., 1995; Morton, 1986; Wee, 1988; Wee & Lee 1980</i>

increased permeability and renders the coating ineffective as a protective layer (Bravery 1988). On the whole, however, plastics are resistant to microbial attack and the major problems of microbial growth are aesthetic, i.e. discoloration of the surface, and, where internal structures such as plastic bathroom fittings are involved, leads to health hazards. Biofilms can harbor pathogenic and toxigenic fungi such as *Aspergillus flavus*, as well as non-pathogenic but allergenic fungal and actinomycete spores. These may be responsible, at least partially, for the so-called sick building syndrome (Raty *et al.*, 1994) which causes the loss of many working days per year in commerce. Such biofilms occur not only in bathrooms, but also on wall and ceiling materials in water damaged rooms (Andersson *et al.*, 1997; Grant *et al.*, 1989) where they can lead to debilitating respiratory problems in the inhabitants of the building. Some of the fungi implicated in the deterioration of building materials are listed in Table 5.

Phototropic microorganisms of paint spoilage

Algae have an important role in the disfigurement of buildings. They are particularly prevalent in shaded areas of high humidity, such as rural environments or more wooded urban areas. The filamentous green alga *Trentepohlia odorata* was the most common colonizer of high-rise buildings in Singapore. This organism typically produces streaks of orange growth on exposed surfaces, the coloration being due to oil droplets stored within the algal cells. However, *Trentepohlia* was not found to be a major colonizer of painted buildings in India and Brazil (Wee & Lee 1980; Joshi & Mukundan 1997; Gaylarde & Gaylarde, 1998b). As algae require little nutrient, being able to produce cell structural materials from CO₂,

inorganic minerals and light, they readily colonize clean surfaces on new buildings. Oil-based paints and certain paint pigments, however, are inhibitory (Johannessen, 1988) and biofilm formation on these materials is considerably delayed, as it is on new concrete, where the pH (~ 12) is too high for microbial growth. After exposure to leaching by rain containing dissolved CO₂, however, the material becomes conditioned and algal and fungal biofilms readily form. The cyanobacteria are often included in the algae. These organisms normally show a distribution similar to algae, but are more resistant to drought and extreme temperatures and are considered to be of greater ecological importance as pioneer organisms than any other bacterial class (Grant, 1982). In the dry environment cyanobacteria induce weathering of stone and rock in the following steps: 1) attachment of cells in small fissures; 2) growth within the fissure; 3) water uptake and expansion of the cell mass, thus exerting pressure within the structure; 4) precipitation of carbonates and oxalates around the cells; 5) opening of the fissure due to these internal pressures; 6) entry of dust, pollen grains etc.; 7) partial death of cyanobacteria cells and establishment of bacteria, fungi and small animals such as mites within the fissure; 8) increasing internal pressure on the superficial layer of the structure leading eventually to its detachment (spalling) (Danin & Caneva, 1990). A wide range of algae and cyanobacteria were isolated from deteriorated stone monuments that showed the penetration of the cells into the upper stone layers (Ortega-Cal *et al.*, 1991). The laboratory fungal cultures isolated from a weathered sandstone church were able to colonize sandstone cubes in the presence of

algal biomass (*Monoraphidium braunii*), and their presence gave rise to different types of detriogenic fungal products (Gomez *et al.*, 1994). Further work is needed to demonstrate the role of these various microorganisms, and their interactions, in the deterioration of buildings. Cyanobacteria have been found to be the dominant photosynthetic microorganisms on painted surfaces in India (Joshi & Mukundan 1997), Brazil and Mexico (Gaylarde & Gaylarde, 1998b). Filamentous cyanobacteria were most common in India; Plectonema was found in 60% of the samples, with Lyngbya and Nostoc being the next most abundant groups, while the only green algae identified from acrylic painted surfaces were the single-celled coccoid algae, Trebouxia and Chlorella. In Brazil and Mexico considerably more coccoid and colonial cyanobacteria were found (Gaylarde & Gaylarde, 1998b) indicating either a basic difference in populations or an important distinction in detection and identification techniques. Gaylarde and Gaylarde (1998a) maintain that their methods are more capable of detecting coccoid and colonial cyanobacteria than the traditional techniques. The phototrophs which have been isolated from disfigured buildings, or have been shown to be capable of biodeterioration (Table 6, 7).

Algae and cyanobacteria are major detriogens of light-exposed surfaces in buildings, their negative effects being aesthetic (soiling) and retention of water, thus predisposing the surface to colonization by potentially more damaging organisms such as fungi, mosses and higher plants (Grant, 1982; Gomez *et al.*, 1994). Hence the treatment and control of these biofilms is important.

Conclusion

There is at present a lack of information on the paint materials relevant to their conservation. It is important therefore to continue research and to share the information with civil engineers, building conservators, conservation scientists and material manufacturers. Pigmented microorganisms, bacteria, fungi and algae, not only cause discoloration of building surfaces but also they can directly cause degradation of the materials through their metabolic activities. This results in the production of biofilms that must be controlled regularly, using non-abrasive and environmentally safe methods, to reduce the impact of microbial activities. Engineers and architects can contribute by creating an awareness of the requirements of detriogenic micro-organisms to the design of constructions, ensuring that susceptible materials are not used in areas favorable for biofilm formation, or are protected by the application of biocides. This review article may therefore serve as a challenge to researchers to continue developing better methods to evaluate painted materials and objects. These methods and techniques will enable researchers to make the colored world more secure and transparent.

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