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Weathering of Roofing Materials-An Overview

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Abstract

An overview of several aspects of the weathering of roofing materials is presented. Degradation of materials initiated by ultraviolet radiation is discussed for plastics used in roofing, as well as wood and asphalt. Elevated temperatures accelerate many deleterious chemical reactions and hasten diffusion of material components. Effects of moisture include decay of wood, acceleration of corrosion of metals, staining of clay, and freeze-thaw damage. Soiling of roofing materials causes objectionable stains and reduces the solar reflectance of reflective materials. (Soiling of non-reflective materials can also increase solar reflectance.) Soiling can be attributed to biological growth (e.g., cyanobacteria, fungi, algae), deposits of organic and mineral particles, and to the accumulation of flyash, hydrocarbons and soot from combustion.

1. Introduction

Roofing materials are exposed to the elements, namely wind, sunlight, rain, hail, snow, atmospheric pollution, and temperature variations and consequently degrade over time. Even the most durable materials are modified by deposition of ambient dust and debris, and may provide an opportunity for colonization by biological organisms such as cyanobacteria, fungi and algae. In this paper, we broadly review how weathering occurs and discuss several engineering strategies that are employed for improving the performance of roofing materials.

We have been engaged in a multi-year project to develop and commercialize cooler, solar-reflective roofing in conjunction with a number of industrial partners. These materials can save energy used for air conditioning and improve occupant comfort. Since reflective white materials are sometimes not suitable from an architectural standpoint, the work has included materials with specified visual colors but with high near-infrared reflectance [1]. This paper is a summary of what we have learned concerning the weathering of roofing materials.

In Section 2 we list the various environmental stresses experienced by roofing, followed in Sec. 3 by a discussion of damage to polymeric materials (plastics, wood) and other organic materials (asphalts, pigments) initiated by the energetic ultraviolet photons in sunlight. Sec. 4 treats effects of high temperatures on roofing materials. Sec. 5 considers effects of moisture, and Sec. 6 discusses soiling by soot and biological growth.

2. Environmental stresses on roofing

a) Sunlight and temperature variations

The energy content of full direct sunlight normally incident on a roof is about 1 kW m^{-2} (1 kilowatt per square meter). There is a compensating longwave radiative cooling effect of about 60 W m^{-2} , because the effective radiant sky temperature is below air temperature. If the roof is insulated on the underside, the heat dissipation by the roof proceeds mainly by convection to the ambient outside air and by emission of thermal radiation. The convection coefficient for heat transfer is *roughly* $12 \text{ to } 20 \text{ W m}^{-2} \text{ K}^{-1}$, with the larger values occurring during windy conditions, and the radiative transfer coefficient for a surface with high thermal emittance is about $6 \text{ W m}^{-2} \text{ K}^{-1}$. Thus the total heat transfer coefficient ranges from about $18 \text{ to } 26 \text{ W m}^{-2} \text{ K}^{-1}$. From these numbers we infer that the temperature rise of a black roof (reflectance 0.05) in full sunlight will be about $34 \text{ to } 50 \text{ K (}^\circ\text{C)}$, [$61 \text{ to } 90 \text{ }^\circ\text{F}$] warmer than the ambient air. For example, our field data show a temperature rise of $35 \text{ K (}^\circ\text{C)}$ [$64 \text{ }^\circ\text{F}$] at solar noon for home demonstrations with asphalt shingles exposed during August in Redding CA.

The temperature rise in sunlight can directly lead to materials degradation. Increased temperature can accelerate deleterious chemical reactions, cause loss of volatile constituents, and soften some polymers. Temperature changes, either gradual or sudden (rain shower on a hot day), cause stresses due to differential thermal expansion.. In fact even a monolithic material such as a sheet of glass experiences stress that can lead to fracture if it is heated to a non-uniform temperature [2].

The photons of which sunlight is composed vary in energy from about 0.5 to 4 electron volts (eV). About 5 % of the energy is in the form of ultraviolet photons with energies larger than 3 eV. These energetic photons can break many chemical bonds, especially in organic materials. For example, plastics, wood and asphalt are all organic materials composed largely of carbon and hydrogen atoms linked into chains, rings, and more complex structures. Most such materials are altered by ultraviolet radiation, usually followed by oxidation.

b) Wind

Wind exerts forces on roofing. Taller structures and more exposed roofing surfaces experience more force. Since the kinetic energy of wind and the resulting pressures scale as the square of the wind velocity, high-wind areas such as the U. S. Florida coastline require particularly careful attention. Beyond the concern for catastrophic failure of

roofing due to wind, periodic vibrations of roofing materials due to wind can lead to material fatigue and crack formation.

c) Moisture: rain, hail, snow, frost, and dew

Rain tends to clean the roof surface. Some roofing materials are formulated to avoid soil adherence and enhance the cleansing effect of rain. Hail is common in some locations. Large size hail causes mechanical roof damage. Where snowfall is important, the roof must be engineered to support the weight of the snow. Hence in some mountain areas highly sloping roofs that shed snow are employed. Freeze thaw cycles are an additional environmental stress. Water expands when it freezes and can therefore enlarge cracks. Dew and/or frost are a nightly occurrence in many climates. The roof temperature falls below the ambient air temperature on clear nights due to the radiative cooling effect. If the relative humidity is high, dew or frost is formed. Water vapor is absorbed by some building materials, particularly wood. Changes in humidity lead to changes in equilibrium water content. As moisture increases, wood swells; drying is accompanied by shrinkage.

d) Atmospheric gases and pollutants

The nitrogen making up most of the atmosphere (78% by volume) is not very reactive chemically. However reaction with oxygen (21%) and water vapor (~ 0.3 - 3%) can cause the formation of various oxides and hydroxides. For example, corrosion products of iron metal include FeO, Fe₂O₃, Fe₃O₄ and FeOOH. Several other important minor atmospheric constituents include oxides of carbon, sulfur, and nitrogen, for example CO₂, SO₂, and NO₂, formed by combustion. When these gases dissolve in water, acids are formed. These acids can promote corrosive chemical reactions. Another pollutant is soot from combustion. Soot is relatively unreactive but is a strong absorber of sunlight. The presence of soot on roofing darkens the color and leads to undesirable solar heating in warm climates.

e) Biological growth

Cyanobacteria, primitive single-cell organisms, are common on roofing in humid areas such as the southeastern and northwestern parts of the United States. The accumulation of dead colonies of these cyanobacteria (sometimes called algae, but now recognized as a distinct group of microorganisms) is visually evident as dark stains on light colored roofing. One reference [3] indicates that the species *Gloeocapsa* is prevalent on damp rocks. Research by a roofing granule company [4] has identified *Gloeocapsa Magma* as the most frequent cause of staining of roofing granules. Doubtless many other species can be present on roofing, including other cyanobacteria, algae, lichens, mildew, moss, etc. A lichen is a symbiotic combination of algae with a fungus; a fungus is a primitive plant-like organism that lacks chlorophyll. Mildew (e.g., on wood) is due to various species of fungus. Other examples of fungi are mushrooms, yeasts, rusts, and molds. Generally, a useful test for identifying biological growth is the application of a fresh bleach solution.

Inorganic stains such as soot and iron oxide are little affected by bleach, but most biological stains are lightened by bleach [5].

3. Photodegradation of polymeric and other organic materials

Many polymeric materials are subject to photodegradation. Energetic UV photons have sufficient energy to disrupt chemical bonds in many materials. Polymers consist of long chains of similar subunits. The absorption of UV energy can cause the breaking and/or crosslinking of the polymer chains, leading to altered chemical and mechanical properties. After disruption of the initial chemical state, the polymers are likely to react with oxygen and/or water vapor causing additional changes. Another type of photodegradation can occur due to photoabsorption by inorganic pigment particles such as TiO_2 . An electron-hole pair is formed in the pigment particle. A photo-excited hole then, for example, can migrate to the particle's surface and cause a deleterious chemical reaction in the polymer. For this reason, white TiO_2 pigment particles intended for outdoor use are usually given thin coatings of passivating layers such as aluminum hydroxide.

Many polymer materials are too readily degraded by UV energy to be used in outdoor applications. Typically, photo-oxidation can be monitored by measuring the infrared absorption near 6 micrometers caused by oxygen-containing carbonyl ($\text{C}=\text{O}$) groups or the absorption near 3 micrometers due to the hydroxyl (OH) group. One strategy for extending polymer lifetimes is to add UV absorbers to scavenge the UV photons. Two common inorganic UV absorber pigments are carbon black and titanium dioxide white. (Both common forms of TiO_2 , rutile and anatase, switch abruptly from non-absorptive to absorptive near 400 nm and therefore, while they are white in the visible spectrum, they are "black" in the UV. Nano-particles of TiO_2 , with particle size much less than 200 nm, are small enough to be transparent in the visible but are still strong UV absorbers.) Another option is to choose particularly durable polymers.

While TiO_2 particles are effective UV absorbers, it should be mentioned in passing that organic tinted colors (mixtures with TiO_2 white) often fade more readily than "mass tones" (colorant without white). Extensive tables documenting this fading of organic pigments may be found in the Pigment Handbook [6]. This observation suggests that the short wavelength part of the visible spectrum (violet, blue) can sometimes be damaging as well.

For polymer coatings on metal roofing, three durable materials are polyester, silicone-modified polyester, and PVDF (polyvinylidene fluoride) [7]. Polyester is inexpensive, and can be used to form hard, scratch-resistant coatings. However, exposure to UV does cause some chalking. (Chalking is due to surface erosion, which produces small particles of polymer, and thereby causes a dark surface to look whiter. An empirical scale of 0 to 10 is sometimes used to characterize chalking [8].). Polyester formulations with longer polymer chains (higher molecular weight) are more UV resistant than shorter chains. Polyester fabrics are also used in roofing (and, in sails for sailboats). Single-ply roofing

membranes include a polyester fabric for mechanical strength. Silicone-modified polyesters can provide somewhat improved chalking resistance and gloss retention relative to unmodified formulations. For factory coating of metal materials (coil coating), PVDF polymers occupy a premium place in the marketplace. Pure PVDF powder is mixed with about 30% acrylic copolymer to aid in dispersion during the coating process. Product specifications [9,10] indicate the weathering performance expected with 10 years 45° south facing Florida exposure: less than 5 ΔE color change (1 ΔE is the threshold for visual discrimination of differences in lightness or color), 50% minimum gloss retention, 8 maximum chalk, 10% maximum film erosion. Fence post exposures in Florida confirm that PVDF-based metal roof coatings are highly durable [11]. The palette of colors exposed by several manufacturers in south Florida prove that the PVDF-based coatings are very resistant to climatic soiling because of the marginal loss in solar reflectance (less than 5%) incurred for 15 to 35 year exposures (Figure 1). Since the PVDF-based metal roof coatings are among the most durable polymeric materials, the above specifications are a good indication of the present day state of the art. The same specifications [9] indicate that accelerated testing procedures do not correlate well with actual outdoor exposure tests.

In most PVDF coating systems a primer coat of a urethane-based polymer is used to ensure good adhesion. As urethanes are readily degraded by UV radiation, it is necessary to ensure that the PVDF topcoat system is a good UV absorber, as can be accomplished with suitable pigments. This is an example of a general strategy. If outer coatings are sufficiently UV absorbing, more UV sensitive materials can be used underneath. For example, the use of high chroma colors in automotive finishes can be enabled with a UV absorbing clear topcoat. Another example is the asphalt shingle. The color bearing roofing granules must absorb UV efficiently so that UV damage to the asphalt is minimized.

Single-ply roofing membranes are usually based on polymer coatings on a polyester fabric. Polymers used include EPDM, PVC, and TPO. EPDM is a synthetic rubber termed ethylene propylene diene monomer. That is, it is three monomers (E, P, and D) polymerized together. PVC is the ubiquitous polymer polyvinyl chloride. TPO is the industry designation for thermoplastic polyolefin. Polyethylene and polypropylene are examples of TPOs. Three types of additives are used to enhance the outdoor stability of single-ply roofing membranes. First, UV absorbing pigments such as carbon black or titanium dioxide white can be added. Also designated as UVA (UV absorber) are special organic compounds such as benzophenone and hydroxyphenyl triazine [12]. The use of UV absorbers, of course, does not protect the surface region of the polymers, because a certain thickness is required to effect absorption. Important additional types of additive that can help protect the polymer including the surface region are hindered amine light stabilizers (HALS). HALS molecules do not themselves absorb UV light, but they react with free radicals (molecular groups with unpaired electrons) formed by UV absorption and thereby interfere with the photo-oxidation process.

One study of accelerated weathering of polypropylene is prototypical of how many polymeric materials change as they weather [13]. The surface region of the polymer

oxidizes during exposure to UV light in air. Infrared spectroscopy on microtomed slices of the polymer quantifies the presence of carbonyl (C=O) groups. While the reaction with oxygen requires the presence of UV light, the extent of oxidation is limited by oxygen diffusion from the surface into the interior. Figure 2 shows how the oxidation proceeded as a function of accelerated testing exposure time. Results for samples containing a UV absorbing additive were similar, but the depth of the penetration of oxygen is diminished. The oxidized surface region is brittle and cracks readily when the polypropylene film is stretched. After longer exposures, the surface region cracks spontaneously, indicating that the oxidized region is both brittle and under tensile stress.

Wood shakes and shingles are popular as roofing in some parts of the world. Wood is largely composed of cellulose, a biopolymer. The cellulose fibers provide strength, and lignin, another biopolymer, acts like an adhesive to bind the fibers into a matrix. Exposure to UV radiation from the sun changes the wood's color, with light colored wood becoming darker, and some darker woods becoming lighter. This color change is attributed to minor components of wood termed (water soluble) extractives [5]. Lignin also yellows on UV exposure [14], which indicates that it absorbs short visible wavelengths, i.e., blue. Exposure to UV also causes damage to the lignin binder, thus leading to detachment of cellulose fibers, and to erosion of the wood surface. Erosion of a number of bare wood samples mounted vertically with south facing exposure was in the range of to 0.2 – 1.3 mm over a ten-year period [5]. Thus the erosion process is slow, although it is somewhat faster for the near-horizontal exposure of wood roofing [15].

An explicit example of the changing reflectance of wood with environmental exposure is shown in Fig. 3 (from our unpublished measurements). The unweathered sample is a reddish brown, as can be inferred from the spectrum. The near-infrared reflectance is quite high. After weathering the reflectance drops (except at short wavelengths), and the resulting color is less reddish, nearly gray.

Asphalt is the key adhesive (binder) material in asphalt shingles. These roofing materials consist of a fiberglass or felt cloth that is saturated with asphalt and additives, and coated with colored roof granules [16,17]. Asphalt serves as an adhesive and as a hydrophobic water proofing agent. Asphalt itself is a complex mixture of hydrocarbons that is a byproduct of the refinement of crude oil into gasoline. In addition to the predominant hydrogen and carbon atoms, some heteroatoms such as nitrogen, oxygen, and sulfur are present. The ease of photo-oxidation of asphalt was illustrated in a study of oxygen uptake in 20 micrometer thick asphalt films [18]. Infrared absorption at 1700 cm^{-1} (5.9 micrometers wavelength) by the carbonyl group (C=O) increased rapidly in just a few hours of full sun exposure. This study also used filters to show that short wavelength UV solar photons (320 nm), while few in number, were much more damaging than longer wavelength UV photons (350 nm). At wavelengths in the visible range (>400 nm), no photo-oxidation was detected. In addition to increased concentrations of C=O groups, photo-oxidation also leads to the increased presence of several types of sulfur-oxygen groups including the sulfate (SO₄) group [19]. As a result of oxidation, asphalt becomes harder and embrittled [19,20]. In order to achieve acceptable weathering lifetimes for asphalt shingles, therefore, it is essential that the roofing granules absorb the UV

component of sunlight. Manufacturers test granules to ensure that they are efficient UV absorbers. Then, if good coverage of the asphalt substrate is achieved by the roofing granules, the photo-oxidation process is largely prevented.

Organic pigments often have high chroma (color intensity) and are desirable for product color formulation. Unfortunately rooftop exposure rules out all but the most durable organics. Application to roof tiles and roof granules, for example, not only exposes pigments to UV, but also to moisture and reactive pollutants such as SO₂ and NO_x. Even some inorganic pigments cannot withstand this weathering. For example ultramarine blue, cadmium sulfide and cadmium selenide react with oxygen; even carbon black fades to some extent. Durability is enhanced if the pigment can be isolated from gases in the environment and, particularly, if the pigment is shielded from the UV. One example of a durable organic pigment in use to color roofing granules is phthalocyanine (“phthalo”) green. The Pigment Handbook [21] assigns phthalo green an exterior durability rating of 4-5 on a scale of 1 to 5 (based on 18 months exposure in Florida) and lightfastness ratings of various formulations in polymer coatings in the range of 6-8 on a scale of 1-8. It is used in roofing granules together with a durable chromium oxide green to produce a brighter color. After time, some fading of the phthalo green occurs, and the roof assumes a more muted color. The Pigment Handbook [6] and the monograph *Industrial Organic Pigments* [22] are useful references on the durability of organic pigments. And, of course, the pigment manufacturers are an excellent source of information of the applicability of pigments for the various specific applications.

The preceding few paragraphs are a very broad overview of the photodegradation of organic materials. This is a mature and complex subject, covered in monographs [23-26] and journals such as *Progress in Organic Coatings*, *Polymer Testing*, and *Polymer Degradation and Stability*. An additional interesting reference is the United Nations’ assessment [27] of effects of increased UV exposure on building materials due to a decrease in ozone levels in the upper atmosphere.

4. Effects of increased temperatures on roofing materials

Usually, the increased temperatures experienced by roofing due to absorption of solar radiation are undesirable from a materials lifetime point of view. Furthermore, roofing materials are commonly believed to be less durable in hotter climates [28]. In this section, we discuss some of the mechanisms by which higher temperatures hasten material degradation. At the outset, however, we must acknowledge that in some cases elevated temperatures are irrelevant or beneficial. Ceramics like clay tile are fired at a high temperature in air during the manufacturing process. If free of reactive and water soluble impurities, these materials are extremely stable and understandably immune to moderate changes in temperature. Pigments that are metal oxides and mixed metal oxides are likewise rather inert. Polymeric materials often have the advantage of flexibility and elasticity, which helps them resist tearing. Exposure to cold temperatures reduces this elasticity and thus can lead to brittle failure. The failure of an O-ring in the space shuttle was a catastrophic example of this problem.

Materials degradation usually involves chemical reactions, and most chemical reactions progress more rapidly at higher temperatures. The phenomenological law describing the temperature dependence of chemical reactions is often attributed to the Swedish chemist Arrhenius [rate proportional to $\exp(-A/T)$, with A a constant and T the absolute temperature]. It is not unusual for reaction rates to double with as small a temperature increase as 10 K (10 °C, 18 °F).

In addition to an inherent temperature dependence of chemical reactions, many degradation processes involve in- or out-diffusion of low-molecular-weight components. Diffusion usually proceeds more rapidly at higher temperature, often with an Arrhenius temperature dependence.

Asphalt shingles

The thermal aging of asphalt roofing shingles provides a good example of effects of oxygen diffusion and reaction with oxygen. For a well-designed shingle, UV photo-oxidation is not likely to be very important since the granules absorb most of the incident UV radiation. For oxidation to occur, atmospheric oxygen must diffuse through the asphalt matrix in order to react in the interior.

Terrenzio *et al.* [29] discuss the thermal aging of the asphalt in roofing shingles as follows: In the diffusional model of asphalt aging, heat first promotes the diffusion of (lower molecular weight) oils out of the bulk of the asphalt. Then, some of the oils evaporate, and others are washed away because of photo-oxidation and subsequent solubility in water. Finally, oxygen diffuses into the system, resulting in the formation of more heptane-insoluble, polar molecules known as asphaltenes. As the aging progresses, these diffusion processes may lead to final failure of the system (typically cracking) as the asphalt becomes harder and stiffer. Further details are provided in a recent publication [30].

The Asphalt Roofing Manufacturer's Association (ARMA) recommends that asphalt shingles not be applied directly over thermal insulation [31]. The basic reason is that (solar) heat build up, which is typically a result of inadequate ventilation, may accelerate weathering and reduce the anticipated life of the asphalt shingles. Thus it is clear that excessively high shingle temperatures are detrimental. Roof venting is useful, and not merely for heat dissipation. It can also avoid moisture build up [32], which is important for many types of roofing. Excessive water vapor and/or condensation lead to swelling and rotting of wood and faster corrosion of metal. Wood shake and tile roofs often incorporate roof underside ventilation as an integral part of the design.

In a study of the aging of paving asphalts [33], the authors concluded that oxidation is a key factor in asphalt hardening in hot climates, and cited further evidence that the rate of thermal oxidation is approximately doubled for every 10 K rise in temperature.

Since photodegradation is a complex process that depends upon material type, including additives and impurities, it is difficult to generalize about how photodegradation should be altered by increased temperatures. Generally, we expect that higher temperatures may assist photodegradation. Here, we will simply cite one example, a study that investigated the durability of unprotected polyethylene [14]. Two sets of samples were exposed to sunlight in Dharhan, Saudi Arabia. One set was maintained at 25 °C, while the other was exposed in outdoor air at higher temperatures. The sample extensibility was measured as a function of time. Extensibility is the extent of elongation before tearing. Samples maintained at 25 °C lost 50% of their original extensibility after 6 mo. Corresponding samples at higher outdoor temperatures reached 50% extensibility after only 2 mo. Thus, in this specific case, photodegradation proceeded more rapidly at highly temperatures.

Thermoplastics such as polyvinyl chloride, polyethylene, and polypropylene become soft and can deform at high temperatures. In hot sunny climates dark colored roofing reaches temperatures approaching the boiling point of water. Manufacturers formulate roofing materials with the maximum roof temperatures in mind, and may restrict the application of certain dark colored materials in hot climates.

5. Effects of moisture

Moisture can cause decay of wood and hasten corrosion of metal. Two other deleterious effects of moisture are efflorescence, a sort of surface staining, and freeze-thaw damage.

“Dry-rot” of wood requires the presence of significant quantities of water. The fiber saturation point, the maximum moisture content reached by wood in humid air but no liquid water, is usually about 25 to 30% by weight. Wood with less than about 20% moisture is considered immune from dry rot [34]. Rot is the result of fungal infection. There are several types of fungi that stain and infect wood, and fungal spores are usually widely dispersed in ambient air. Surfaces infected with actively growing fungi show thread-like features (hyphae) under microscopic examination. Some species of fungi consume just the cellulose portion of wood, some the lignin, still others both primary wood components. After decay, the wood is much less dense and fractures readily. After sufficient fungal growth, fruiting bodies such as toadstools form that release new spores into the air.

Corrosion of metals is caused by chemical reactions with environmental substances, particularly the formation of metal oxides. Rusting of steel is a prototypical example. Modern steel used in roofing generally has a protective, sacrificial coating of zinc or a zinc-aluminum alloy to prevent rust. Then the metal alloy is further protected from chemical reactions with a polymeric coating. Nevertheless, most metals occur in mineral form only as combinations such as metal oxides, hydroxides, sulfides, carbonates, etc., and tend to revert to their mineral forms over time. Many of the corrosive reactions involved are electrochemical in nature and require the presence of an aqueous electrolyte – a solution of salts in water. Liquid water may be in direct contact with the metal in question or may be extracted from moist air due to the presence of hygroscopic dust. Thus it is not surprising that metallic corrosion proceeds more rapidly in humid climates

in which moisture is readily available [35]. Also, it is noteworthy that dissolved salts increase the electrical conductivity of water, making it a more effective electrolyte. This may be the primary reason that seaside salt air promotes corrosion.

Efflorescence is the occurrence of light colored stains on the surface of a porous material. It is caused by water seepage/diffusion through the material. Dissolved salts are transported along with the water, and are deposited on the surface when the water evaporates. A test for potential efflorescence of clay roof tiles is to immerse one end of the tile in distilled water for seven days in a drying room [36], and then inspect for staining. Efflorescence is a common issue for concrete items, particularly if they are dark in color. Water transports calcium hydroxide to the surface, and calcium carbonate is then formed by reaction with the CO_2 in air [37]. These white deposits can be prevented by the use of a polymeric coating that seals the surface [38]. Alternatively, the deposits can be removed by washing with dilute acid. If left in place, the calcium carbonate stains often weather in about 2 years, restoring the original appearance.

Freeze-thaw cycles are associated with the spallation of concrete and the premature failure of clay tiles. For this reason, ASTM standards for clay roof tile limit the permissible water absorption by the tiles [36]. For grade 1 tile, that provides resistance to severe frost action, maximum cold water absorption is limited to 8 % in any one tile and to 6 % average in a sample of 5 tiles. For grade 3 tile, that provides negligible resistance to any frost action, the permissible water absorption values are about twice as large.

6. Soiling of Roofing

Deposits on roofing originate with dry and wet (rainwater) deposition from the atmosphere. Clearly, one expects crustal dust (soil) to be present. Products of combustion such as soot, unburned hydrocarbons, and fly ash are expected as well. Sea salt is expected (in coastal areas) as are organic compounds emitted by vegetation (such as terpenes) and spores produced by plants and fungi. Due to the cleansing effects of rainwater, one expects that deposits on roofing may be depleted of water-soluble components. Of course rainwater can also transport small insoluble particles as well.

Suppose a substrate has a clean reflectance denoted R_0 , which is coated with a thin uniform soil layer with absorptance a and reflectance r . In view of the assumption that the layer is thin, we take both a and r as small compared to unity. (The extension to thicker soil layers is straightforward, for example, by recursion.) Then, it is not difficult to show that the change in reflectance R of the soiled substrate is given, to first order in r and a , by $R - R_0 = -2 R_0 a + (1 - R_0)^2 r$. Thus soil absorptance reduces R and soil reflectance increases R . Here we can also see that a will be more important if R_0 is large and r will be more important if R_0 is close to zero. Thus we expect that highly reflective materials tend to lose their reflectance as they are soiled, with the reflectance loss determined by absorption of the soil. Very dark materials tend to become lighter as they are soiled, with the reflectance increase caused by light scattering by soil. Finally, if the ratio r/a is such that $2 R_0 a = (1 - R_0)^2 r$, then $R - R_0 = 0$ and soil deposits do not change the reflectance.

M. Ebert *et al.* [39] studied airborne aerosols in the size range of 0.1 to 25 micrometers, collected in Germany, by means of high resolution scanning electron microscopy and energy-dispersive X-ray microanalysis. By combining particle morphology data with chemical microanalysis, they recognized several characteristic particle types. Particles of silica and mixed oxides of silicon and aluminum were common, and appeared to have two distinct origins. Large irregular fractured particles were thought to be crustal in nature, whereas spherical particles in the sub-micron and micron size range were identified as fly ash. Particles were classified as metal oxides/metal hydroxides if they were low in silicon content and contained additional metals such as Fe, Mn, Zn, Al, Ti, Cu, Ni, and Pb. These particles could likewise be spherical fly ash or irregular dust particles. Calcium sulfate particles could be identified by the high Ca and S content and a plate-like morphology. Soot particles were identified by their fractal-like morphology: branched chains of ~ 50 nm spheres. Some biological particles had recognizable morphologies, such as fungal spores. Other biological particles were identified by $>25\%$ C, plus characteristic signatures of the minor elements Na, Mg, P, S, Cl, K, and Ca. Two further particle types were sea salt and ammonium sulfate, both of which are water soluble and will not be discussed further here.

Overall, of the elements heavier than sodium (Na), the most abundant elements were Al, Si, and S. Elements present in roughly ten times lower concentration were Na, Mg, P, Cl, K, Ca and Fe. Other elements were even less abundant. If the lighter elements had been detectable in this particular analysis, we would expect to see large contributions from H, C, N, and O as well.

The optical properties of the aerosols in the particle size range 0.1 to 3 μm were compiled based on an analysis of the phase composition of the particles. The complex refractive index thus derived is useful in computing light scattering and absorption in the atmosphere, and by extension may be useful in the optical properties of deposits on roofing. They found that the real part ranged from 1.54 to 1.72 and the imaginary part from 0.001 to 0.086. The lower values were associated with unpolluted rural air masses, and the higher values, with polluted urban air. The higher values of the real part are identified with higher concentrations of the metal oxide/hydroxide particles, and the higher values of the imaginary part are identified with increased concentrations of soot. If the imaginary part is zero, optical absorption is absent; only scattering occurs. Thus soot is the primary absorber in atmospheric aerosols.

As part of our present ongoing investigation on solar-reflective roofing, we have examined deposits that have formed on exposed roofing samples at several locations in California [40]. Selected results are shown in Table 1. Since the samples were taken in the spring, after California's winter rainfall, the deposits were affected by rainfall and are less extensive than would have been the case if the samples were obtained in September, after the dry California summer. Thus the observed solar reflectance values were about the same as for unsoiled samples. For example, three samples with initial solar reflectance of 0.57 had reflectance of 0.54 ± 0.02 after 19 months. Sulfur is not found in high abundance, which may be attributed to the absence of coal-fired power plants in

California. Calcium is found in rather high abundance, except for the remote McArthur site in northeastern California. Due to the small amount of sulfur present, the calcium is likely to be in the form of carbonate (rather than sulfate). The first five metals in Table 1 all have white oxides, and are unlikely to reduce the reflectance of highly reflective roofing. (They are, of course, expected to raise the reflectance of black roofing.) The relatively abundant transition metals Fe, Mn, Cu, Cr, have colored or black oxides and other compounds and therefore may reduce roof reflectance slightly. Of these elements, iron is the most abundant. To obtain a semi-quantitative estimate of the maximum possible optical absorption of the iron, we can assume that $\sim 60 \text{ mg m}^{-2}$ are present in the form of strongly absorbing small ($0.27 \text{ }\mu\text{m}$ diameter) hematite (Fe_2O_3) pigment particles. Hematite is a strong absorber of the short wavelength part of the solar spectrum (300 to 550 nm) with a coefficient of roughly $4 \text{ m}^2/\text{gm}$ [41]. Thus such a hematite layer could absorb a measurable portion ($\sim 20 \%$) of the short wavelength component. Most likely, however, the iron mineral particles present are in the form of larger particles that are less efficient than the sub-micrometer particles of our example.

The role of elemental carbon (i.e., soot) is potentially more dramatic. Figure 4 shows the expected [42] solar reflectance and visible reflectance as a function of soot concentration, as a fraction of the high initial reflectance R_0 . The sample exposed at Richmond has the most elemental carbon (1.3 mg m^{-2}), but this amount is insufficient to markedly reduce its reflectance.

Like hematite, the effect of organic carbon is expected to be largest at shorter wavelengths, but published absorption coefficients (roughly $0.6 \text{ m}^2 \text{ g}^{-1}$ at 550 nm) [43] suggest that it is less important than elemental carbon ($\sim 14 \text{ m}^2 \text{ g}^{-1}$ at 550 nm) [43] for equivalent masses per unit area.

As far as biological growth on roofing surfaces is concerned, it is clear that a large variety of species is expected to be present. For example, some of the species of fungi that occur in soil may be expected to be present. However, the ultraviolet radiation incident on roofing can kill many organisms. We have noted earlier that the cyanobacteria *Gloeocapsa* infests mineral roofing granules, leading to black colored stains. In a study of biomass accumulation on single ply roofing membranes exposed in Oak Ridge, Tennessee [44], it was found by phospholipid fatty acid analysis that the biological growth was in this case primarily fungal in nature.

C. C. and P. M. Gaylarde [45] recently published a study of 230 biofilms found on the exterior of buildings in Europe and in Latin America. They classified the biofilms according to the predominant microscopic organisms found, of which the most important were various cyanobacteria, algae, and fungi. The substrate was important with, for example, fungi rarely found on mineral substrates and often on paint. Climate was believed to be important as well, with algae more prevalent at cool damp European sites and dark-colored cyanobacteria frequently found in tropical locations at elevations above 1000 m.

Dupuy [46], as cited by Ortega-Calvo [47], investigated the cyanobacteria that grew on monuments exposed to strong solar radiation and that could tolerate long dry periods. They include *Calothrix parietina* and *Chroococcus montanus* as pioneer species, which are followed by species of *Gloeocapsa*, *Nostoc* and *Scytonema*.

In a detailed study of the fungal colonization of plasticized PVC outdoors in Manchester, United Kingdom, Webb *et al.*[48] used gene sequencing to definitively identify several of the species involved. The fungus *Aureobasidium pullulans* had the ability to extract metabolic carbon from the plasticiser in the intact PVC formulation, and was thereby able to initially colonize the surface after 25 – 40 weeks. Subsequently, a group of yeasts and yeast-like fungi, including *Rhodotorula aurantiaca* and *Kluyveromyces* spp., established themselves on the PVC after 80 weeks of exposure. In addition to *A. pullulans*, many of the observed fungi, e.g., *Alternaria* spp., *Aspergillus* spp., *Paecilomyces* sp., and *Cladosporium* sp., have previously been isolated from deteriorated PVC and are common colonizers of painted surfaces and building materials.

In the roofing industry it is often not known exactly what species make up the biomass deposits on roofing. In fact, the terms algae and fungi are sometimes used interchangeably. However, it is well known that in humid climates, such as the southeastern United States, the growth of biomass on roofing leads to visible stains. In some cases, it has been noted that staining does not occur near copper and galvanized (zinc) flashings. In a patent by Narayan *et al.*, [49] reviewing prior art, it is noted that algae growth on asphalt shingles can be inhibited by metal Zn particles, ZnO, ZnS, and cuprous oxide (Cu₂O). Thus it appears that zinc and copper ions can inhibit biological growth. A more recent patent [50] likewise discloses that Cu₂O, either alone or with zinc compounds, is effective in roof granules, to prevent growth of cyanobacteria (such as *Gloeocapsa*) and also fungi.

Levinson *et al.* [51] investigated a number of light-colored PVC roof membranes that had been exposed for a number of years and that had obvious biological growth, presumably fungal in nature. The spectral reflectance was measured both before and after a number of cleaning procedures. In this way inferences could be made concerning the spectral absorbance of the substances removed. Three different types of spectra were observed. First, optically thick black spots of biomass were found. Second, “organic carbon” with a spectrum similar to that in [43] was found. Third, “soot” with a broadband spectrum similar to that shown in [42,43] was found. In this study of PVC roof membranes, it was found that only partial cleaning can be performed by the use of soap and water, but that bleach is effective in removing residual stains.

Biocides are often included in the formulation of polymeric materials such as PVC. As just one example, the compound OIT (2-n-octyl-4-isothiazolin-3-one) is used commercially for this purpose. Concentrations on the order of 10 ppm inhibit the growth of a number of common fungi [52]. However, premature leaching is an issue that must be addressed in material formulation.

7. Summary

We have presented an overview of the weathering of roofing materials. Emphasis has been placed on chemical changes and changes in visible and solar reflectances. Photodegradation is very important for organic materials: plastics, wood, asphalt and organic pigments. Photodegradation is initiated by energetic UV photons in sunlight and generally involves chemical reactions with atmospheric oxygen and/or water vapor, leading to brittleness. Elevated temperatures, for example as provided by solar absorption in dark materials, lead to acceleration of deleterious chemical reactions and can hasten the diffusion of low molecular weight components. Moisture is also a key factor in many degradation processes. For example, corrosion of metals is accelerated by high humidity. Deposits that form on roofing include the various atmospheric aerosols such as crustal dust, soot and hydrocarbons from incomplete combustion, and organic particles including spores. Biological growths on roofing include cyanobacteria on roofing granules, algae on mineral materials in cool damp climates, and fungi on polymeric materials.

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References

[1] R. Levinson, P. Berdahl, H. Akbari, W. Miller, I. Joedicke, J. Reilly, Y. Suzuki, and M. Vondran, Methods of creating solar-reflective nonwhite surfaces and their Application to residential roofing materials, *Sol. Energy Mater. Sol. Cells*, in press (2006).

- [2] A. A. Joshi and P. J. Pagni, Fire-induced thermal fields in window glass. II – Experiments, *Fire Safety Journal* 22, 45-65 (1994).
- [3] Web page of T. Futchler, Columbia Union College, Takoma Park, Maryland, <http://www.cs.cuc.edu/~tfutchler/Cyanophyta.html>.
- [4] Web page for 3M roofing granules, http://solutions.3m.com/wps/portal/_l/en_US/_s.155/115625/_s.155/117267.
- [5] R. S. Williams, The finishing of wood, Chapter 15 of Wood handbook-Wood as an engineering material, Forest Products Laboratory, Madison, Wisconsin (1999; available online).
<http://woodworking.about.com/gi/dynamic/offsite.htm?site=http://www.fpl.fs.fed.us/>
- [6] *Pigment Handbook, Vol. I, Properties and Economics*, 2nd Ed., P. A. Lewis, Editor, John Wiley & Sons, New York (1988).
- [7] R. Reed, Painted metal: From fluoropolymers to polyesters, sorting out the issues in coil coatings, in *Metal Roofing* (August-Sept. 2003).
- [8] ASTM Standard D 4214 – 98, Standard test methods for evaluating the degree of chalking of exterior paint films, published by ASTM International, West Conshohocken, PA 19428-2959, United States (1998).
- [9] ASCA 96 specification as listed at http://www.products.arkemagroup.com/pdf/techpoly/ASCA_96.pdf.
See also Arkema, ATOFINA Chemicals, Inc., Philadelphia, product brochure on Kynar 500 PVDF resin-based metal coatings. Cited ASTM standards are Hunter color change D 2244, chalking D 4214 and D 659, and gloss D 523.
- [10] P. P. Greigger and P. Wilson, High-performance fluoropolymers coatings, PPG Industries, Springdale, PA, article on website at corporate.ppg.com/ppg/paf/documents/corwhite.doc
- [11] W. A. Miller, S. Kriner, and D. S. Parker, Cool metal roofing is topping the building envelope with energy efficiency and sustainability. *RCI Foundation conference, "Cool Roofs: Cutting through the glare."* (Atlanta, CA, May 12-13, 2005).
- [12] Website of Ciba Specialty Chemicals (<http://www.cibasc.com/>), subject of Light Stabilizers.
- [13] G. E. Schoolenberg and P. Vink, Ultraviolet degradation of polypropylene: 1. degradation profile and thickness of the embrittled surface layer, *Polymer* 32, 432-437 (1991).

- [14] A. L. Andrady, S. H. Hamid, X. Hu, and A. Torikai, Effects of increased solar ultraviolet radiation on materials, *J. of Photochemistry and Photobiology B: Biology* 46, 96-103 (1998).
- [15] M. Knaebe and C. Carll, Wood shakes and shingles for roof applications; tips for longer life, Forest Products Laboratory finishing factsheet, US Dept. of Agriculture Forest Service (January, 1998).
- [16] H. Akbari, R. Levinson and P. Berdahl, Review of residential roofing materials, Part I: a review of methods for the manufacture of residential roofing materials. *Western Roofing Insulation and Siding*, 54-57 (Jan/Feb, 2005).
- [17] H. Akbari, R. Levinson, and P. Berdahl, Review of residential roofing materials, Part II: a review of methods for the manufacture of residential roofing materials. *Western Roofing Insulation and Siding*, 52-58 (Mar/Apr, 2005).
- [18] Y. Tropsha and A. Andrady, Photodegradation of asphalt and its sensitivity to the different wavelengths of the sunlight spectrum, in *Polymeric Materials Science and Engineering*, Vol. 66, Spring Mtg. of the Amer. Chem. Soc. Division of Polymeric Materials, p. 305 (1992).
- [19] J. Huang, R. Yuro, and G. A. Romeo, Jr., Photooxidation of Corbett fractions of asphalt, in *Fuel Science and Technology Int'l.*, 13, 1121-1134 (1995).
- [20] J. C. Petersen, A dual, sequential mechanism for the oxidation of petroleum asphalts, *Petroleum Science and Technology* 16, 1023-1059 (1998).
- [21] R. Pascoe, Phthalocyanine green pigments, Chapter I-D-1-2, Table 5, in *Pigment Handbook, Vol. I, Properties and Economics*, 2nd Ed., P. A. Lewis, Editor, John Wiley & Sons, New York, 1988.
- [22] W. Herbst and K. Hunger, *Industrial Organic Pigments*, Wiley-VCH, Weinheim, Germany, 1998.
- [23] *Handbook of Polymer Degradation*, Hamid, S.H., Amin, M.B. and Maadhah A.G. (eds), Marcel Dekker Inc. New York. (1995).
- [24] Rabek, J.F., *Polymer Photodegradation*, Chapman and Hall, London, England. (1995).

- [25] Scott, G.. *Polymer Degradation and Stabilization*, Elsevier Applied Science Publishers, London (1990).
- [26] Wypych, J., *Weathering Handbook*, 2nd edition, Chemtec Publishing, Toronto, Canada (1995). Despite the title, this reference is exclusively concerned with polymers.
- [27] Andrady, A. L., S.H. Hamid, X. Hu, and A. Torikai, Effects of increased solar ultraviolet radiation on materials, Chapter 7 in *Environmental Effects of Ozone Depletion, 1998 Assessment of the United Nations Environmental Programme*. Available online at <http://www.gcric.org/UNEP1998/>.
- [28] C. G. Cash, "Estimating the durability of roofing systems," in *Durability 2000: Accelerated and Outdoor Weathering Testing*, STP 1385, W. D. Ketola and J. D. Evans, eds., American Society for Testing and Materials, Philadelphia, Pa., 165–169 (2000).
- [29] L. A. Terrenzio, J. W. Harrison, D. A. Nester, and M. L. Shiao, Natural vs. artificial aging: use of diffusion theory to model asphalt and fiberglass-reinforced shingle performance, Proc. 4th Int. Symp. on Roofing Technol. 66-74 (Gaithersburg, Sept. 1997).
- [30] M. L. Shiao, D. A. Nester, and L. A. Terrenzio, On the kinetics of thermal loads for accelerated aging, *Roofing Research and Standards Development, 5th Volume*, ASTM STP 1451, W. J. Rossiter and T. J. Wallace, Eds. (ASTM International, West Conshohocken, PA, 2003).
- [31] ARMA Technical Bulletin, Application of asphalt shingles over insulation or insulated decks, ARMA Form No. 209-RR-86. Revised July, 1996.
- [32] ARMA Technical Bulletin, Ventilation and moisture control for residential roofing, ARMA Form No. 211-RR-94. Revised Nov., 1997.
- [33] G. R. Kemp and N. H. Predoehl, A comparison of field and laboratory environments on asphalt durability, *Asphalt Paving Technology* 50, 492-555 (1981).
- [34] M. C. Baker, Decay of wood, Canadian Building Digest, CBD-111, originally published in 1969, <http://irc.nrc-cnrc.gc.ca/cbd/cbd111e.html>.
- [35] Corrosion of zinc, "Knowledge Article" from www.Key-to-Metals.com
- [36] ASTM Standard C 1167-03, Standard specification for clay roof tiles.
- [37] G. Buchner and U. Kundgen, Bayer AG, An anniversary - 25 years of outdoor weathering of pigmented building materials, *Betonwerk + Fertigteile Technik* (July, 1996).

- [38] Bayer Chemicals, Inorganic Pigments Group, Reduction of efflorescence on concrete paving blocks by impregnation with a plastic emulsion, Technical Information from Bayer AG (May, 2002). Also, Removing efflorescence and soil from the surface of concrete pavers (May, 2002).
- [39] M. Ebert, S. Weinbruch, P. Hoffmann, and H. M. Ortner, The chemical composition and complex refractive index of rural and urban influenced aerosols determined by individual particle analysis, *Atmospheric Environment* 38, 6531-6535 (2004).
- [40] M. D. Cheng, W. A. Miller, P. Berdahl, and S. Pfiffner, Composition and effects of atmospheric particles on the performance of steep-slope roofing materials, in preparation.
- [41] R. Levinson, P. Berdahl, and H. Akbari, Solar spectral optical properties of pigments – part II: survey of common colorants, *Sol. Energy Mater. Sol. Cells* 89, 351-389 (2005), Fig. 1, Film R03.
- [42] P. Berdahl, H. Akbari, and L. S. Rose, Aging of reflective roofs: soot deposition, *Appl. Optics* 41, 2355-2360 (2002).
- [43] Thomas W. Kirchstetter, T. Novakov, and P. V. Hobbs, Evidence that the spectral dependence of light absorption by aerosols is affected by organic carbon, *J. Geophysical Research-Atmospheres* 109, (D21): Art. No. D21208 (NOV 12, 2004).
- [44] W. A. Miller, M. D. Cheng, S. Pfiffner, and N. Byars, The field performance of high-reflectance single-ply membranes exposed to three years of weathering in various U. S. climates, Oak Ridge National Laboratory report prepared for, and available from, the Single-Ply Roofing Institute, Needham, MA (2002).
- [45] C. C. Gaylarde and P. M. Gaylarde, A comparative study of the major microbial biomass of biofilms on exteriors of buildings in Europe and Latin America, *Int. Biodeterioration & Biodegradation* 55, 131–139 (2005).
- [46] P. Dupuy, G. Trotet and F. Grossin, Protection des monuments contre les cyanophyces en milieu abrite et humide, in R. Rossi-Manaressi (Ed.), *The Conservation of Stone I*, Centro per la Conservazione delle Sculture all'Aperto, Bologna, 205-219 (1976).
- [47] J.J. Ortega-Calvo, X. Ariiio, M. Hernandez-Marineb, and C. Saiz-Jimenez, Factors affecting the weathering and colonization of monuments by phototrophic microorganisms, *Science of the Total Environment* 167, 329-341 (1995).
- [48] J. S. Webb, M. Nixon, I. M. Eastwood, M. Greenhalgh, G. D. Robson, and P. S. Handley, Fungal colonization and biodeterioration of plasticized polyvinyl chloride, *Applied And Environmental Microbiology* 66, 3194–3200 (2000).

[49] S. B. Narayan et al., Method of inhibiting algae growth on asphalt shingles, U. S. Patent No. 5,356,664 (1994).

[50] I. B. Joedicke, U. S. Patent Application 2004110639 A1 (June 10, 2004}.

[51] M. R. Levinson, P. Berdahl, A. A. Berhe, and H. Akbari, Effects of soiling and cleaning on the reflectance and solar heat gain of a light-colored roofing membrane, *Atmospheric Environment* 39, 7807–7824 (2005).

[52] L. Coulthwaite, K. Bayley, C. Liauw, G. Craig, J. Verran, The effect of free and encapsulated OIT on the biodeterioration of plasticised PVC during burial in soil for 20 months, *Int. Biodeterioration & Biodegradation* 56, 86–93 (2005).

California location	Shafter	McArthur	Sacramento	El Centro	Corona	Colton	Richmond
Coordinates	35.50N 119.27W	41.02N 121.65W	38.59N 121.51W	32.79N 115.56W	33.88N 117.56W	34.07N 117.31W	37.94N 122.34W
Aluminum	16.	5.3	50.	21.	41.	39.	27.
Calcium	17.	1.0	5.6	87.	55.	96.	146.
Silicon	6.8	2.3	9.8	20.	19.	14.	9.7
Magnesium	9.0	0.51	6.1	20.	20.	20.	16.
Zinc	7.3	3.2	52.	1.8	4.4	1.3	1.1
Sulfur	1.4	<1	7.3	<2	1.8	1.2	1.7
Iron	32.	5.0	42.	33.	68.	67.	44.
Manganese	0.28	0.03	0.35	0.6	1.5	3.3	0.9
Copper	0.8	0.3	0.76	1.4	1.4	1.1	0.9
Chromium	1.3	0.7	7.7	0.15	0.6	0.7	0.8
Organic carbon	5.6	1.3	4.5	8.3	5.4	6.1	11.
Elemental Carbon	0.4	~ 0.02	0.22	0.24	0.24	0.16	1.3

Table 1. Concentration of several abundant elements and organic/elemental carbon in mg m^{-2} , collected on samples of roofing materials exposed for 19 months (until April, 2005) at several California locations [40].

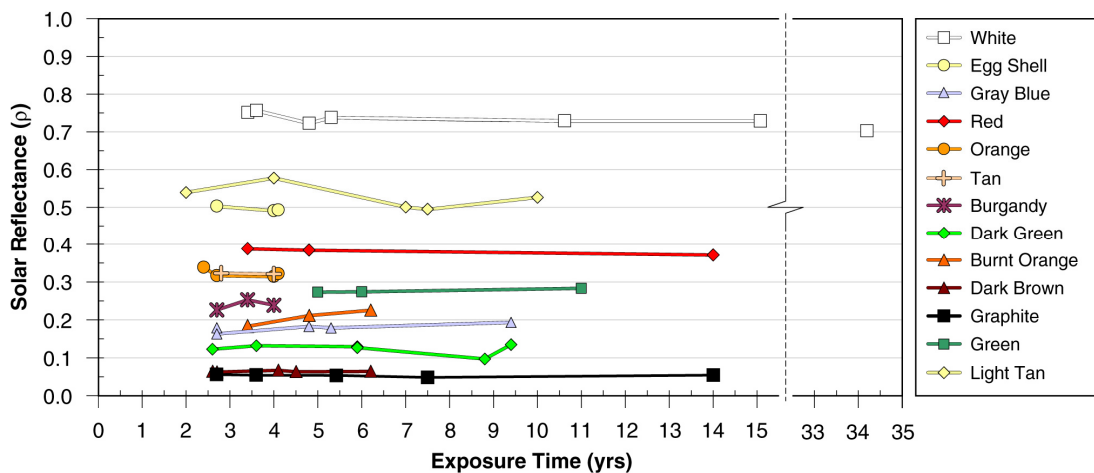


Fig. 1. Solar reflectance of PVDF painted metals acquired from south Florida field exposures for BASF, Atofina, Akzo Nobel and Solvay Solexis.

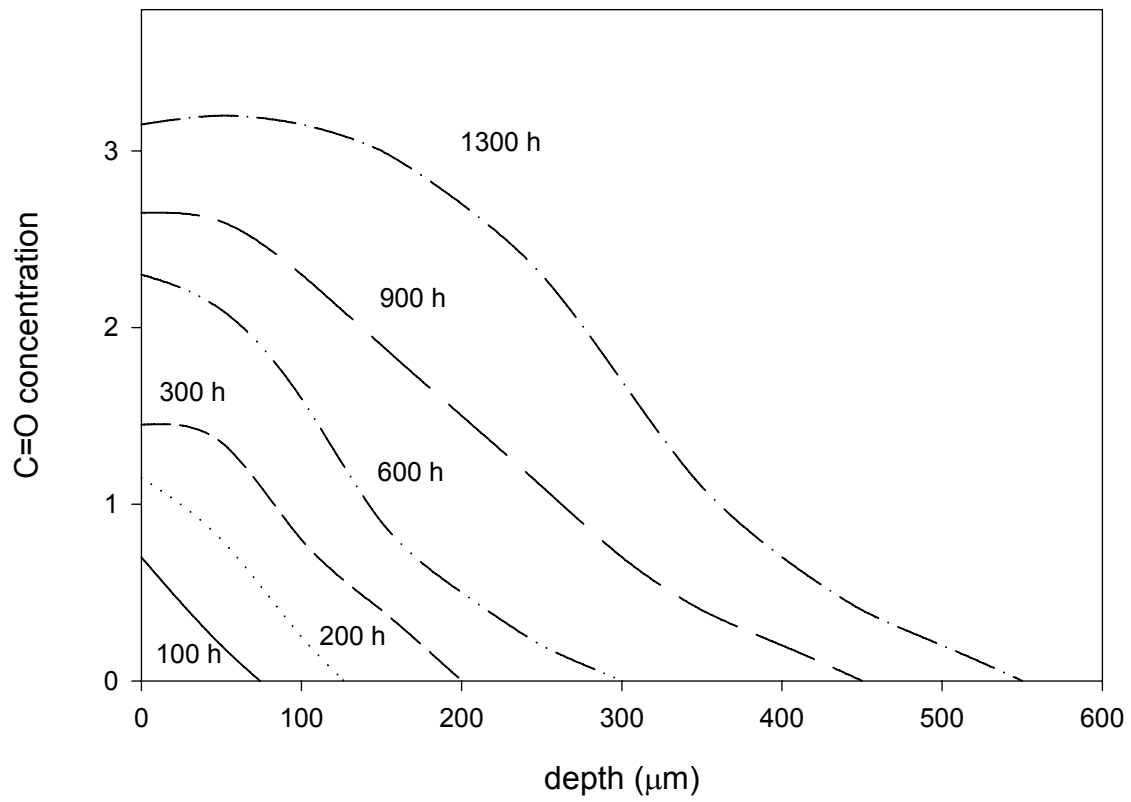


Fig. 2. Oxidation (carbonyl) profiles measured during accelerated UV aging of polypropylene, after [13].

Spectral Reflectance of Western Red Cedar Roofing Shingles
(fire retardant chemically pressure treated)

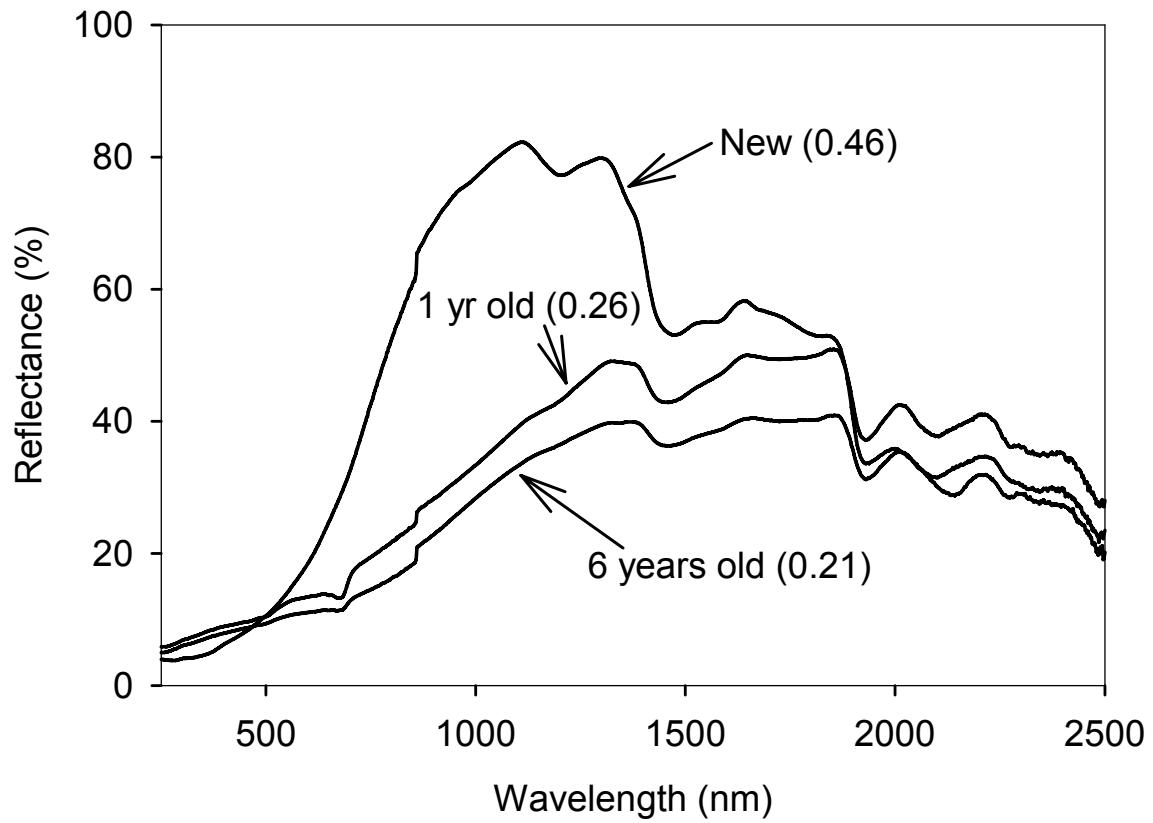


Fig. 3. Spectral reflectance of western red cedar roofing shingles. The solar reflectance is 0.46 when new, and declines to 0.21 after 6 years exposure.

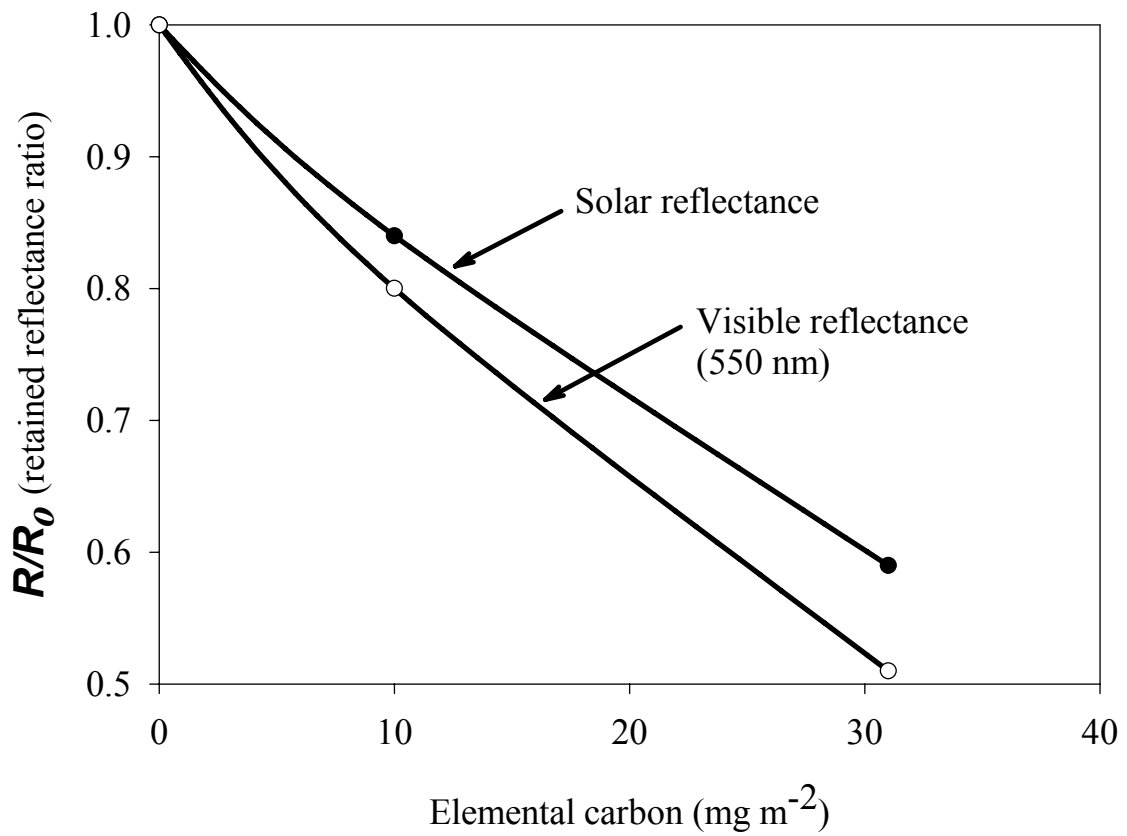


Fig. 4. Expected values for the soiled roof reflectance, divided by the unsoiled reflectance, as a function of elemental carbon (soot) concentration. After [42].