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An Investigation into the Mechanism of Degradation of Domestic Coatings for the Protection of Wood

by

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- PRA, Teddington, Middlesex
- The author's house, Ashford Common, Middlesex

Chemical structures were drawn using ISIS™/Draw Revision 1.2W.

Abstract

Seven coatings intended to represent currently available coatings for wood were exposed to natural weathering, and the changes in them were investigated after various periods of exposure. Four of the coatings were solvent borne, and three water borne. Of the solvent borne coatings, three were based on a flexible alkyd resin, but with different pigments, and the fourth on a traditional alkyd resin. Two of the water borne paints were based on the same acrylic resin, with different pigments, and the third on an alkyd-acrylic hybrid resin.

Each paint was studied by:
  differential scanning calorimetry;
  dynamic mechanical scanning calorimetry;
  Fourier transform infrared - photoaccoustic spectroscopy;
  determination of non-volatile content;
  determination of water extractable material content;
  determination of dichloromethane extractable material content;
  and determination of organic content.

It was found that paints with an alkyd component underwent an immediate additional cross-linking reaction, despite being allowed to cure for at least a month before being placed outside. Iron oxide was found to lower the glass transition temperature in both the autoxidation process and the photodegradation of an alkyd resin when compared with an unpigmented version.

For all coatings, the rate of degradation was dependent on seasonal changes, for alkyds being greater in the summer months, and for acrylics, a change in the polymer backbone was seen after the coating had cycled through its T_g.

Paints with an acrylic component lost material during the first four months of exposure, and this material is thought to be, at least in part, additives (e.g. thickeners).

Contents

1. Introduction

Prior to the 1980s, opaque solvent borne coatings were used extensively to protect exterior woodwork. In the 1980s use of semi-transparent wood treatments became fashionable. Water borne coatings (both opaque and semi-transparent) were also introduced in a response to environmental concerns. Despite careful product development, some of these new products experienced premature failure. In 1982 the DoE estimated the annual expenditure on the protection of exterior woodwork to be £300M in the UK, and so considerable cost savings can be achieved if the lifetime of the coating can be extended.

In 1990 the PRA (Paint Research Association) was commissioned to undertake a study into the causes of premature failure, with the aim to extending periods between maintenance painting. That work was funded by the DTI, the PRA Member Research Programme and the following industrial sponsors:

Akzo Coatings
Butinox Timber Finishes
Cementone Beaver
Coutaulds Coatings
Cray Valley Products
Cuprinol
DSM Resins
GORI all wood International
Hickson Timber Products
ICI Paints
Jotun
Kalon
Manders Paints
Protim Solignum
Rhone Poulenc
Rohm and Haas
Tioxide Specialities
Zeneca Resins

This study was unique in that it studied the three zones where degradation occurs, namely the coating, the coating/wood interface and the wood surface. Collaborative research projects at Imperial College in London, and at University College North Wales were established to investigate changes in the upper region of the wood, up to the wood/coating interface. Additionally, the Finishes Section (Timber Research) of the Building Research Establishment acted as consultants.

The work at Imperial College concentrated on the nutritional requirements of *Aureobasidium pullulans* (the micro-organism commonly responsible for “blue stain” of timber in service). Most micro-organisms cannot directly attack undegraded wood, but weathering of the surface converts the wood into a food source. Changes to the wood surface can initiate coating failure.

The photodegradation of the wood surface was studied by University College North Wales, using a physico-chemical approach. They focused on the physico-chemical factors that initiate loosening of the ligno/polysaccharide structure and the conversion of polysaccharides to simple sugars.

At PRA, a series of chemical, microbiological and physical tests were performed on the coatings. The results of those experiments, and a summary of each of the university reports is published elsewhere[1]. The work described here formed part of that project, but the results were not presented in full.

2. Paint - an overview

A basic paint contains many components. Historically, there are two main components[2], the resin (or binder) and the pigment. Additionally, other components need to be added for the paint to become usable, namely solvent and additives[3]. These components are dictated by the formulation requirements of the coating.

2.1. Formulation requirements

Paints are formulated with a specific purpose in mind. The factors governing the formulation are[2]:

- substrate
- pretreatment
- physical properties of paint
- application techniques
- drying time
- durability
- toxicity
- cost
- specifications
- special factors

2.1.1. Substrate

The substrate is the surface to which paint is applied for the purpose of protection or decoration, or both. Common substrates include wood, masonry, metal and plastics.

Rather obviously, a paint for a wooden window must have very different physical properties from that for, say an iron bridge. Wood expands and contracts with different water concentrations, and so a coating on wood needs to be flexible. Additionally, windows will be opened and closed, and so the paint must not stick to itself once it has dried (this property is termed the blocking resistance). A wooden window may mean that the substrate is either new wood, old but sound wood, or previously applied paint. Wood that has been exposed to natural weathering for more than two weeks is generally regarded as unsuitable to receive paint without sanding back to fresh wood[4]. Even if such preparation is carried out, Boxall and Smith[5] found that the coating is more likely to fail than if the coating was applied to new wood.

2.1.2. Pretreatment

In our wooden window example, the substrate will have one of two preparations, namely light sanding for wood, or cleaned ("rubbed down") old paintwork. For a topcoat for wood, pretreatment will also include the use of an appropriate primer and undercoat.

2.1.3. Physical properties of paint

Not only does the substrate govern properties to be incorporated into the paint, but decorative and protective requirements must also be met. So, for our wooden window example, the colour, the level of gloss, the opacity, and whether the coating is supposed to exclude water from getting into the wood (or whether it is going to let the wood "breathe"), must all be designed into the paint at the formulation stage.

2.1.4. Application techniques

Even for wooden windows, very different coatings can be made for different application requirements. A factory applied product can utilise methods such as dip tanks (where the substrate is immersed in the paint and withdrawn - the coating thickness being adjusted by the rate of withdrawal), curtain coatings (where the substrate is passed under a "waterfall" of the coating), spray (where the coating is applied as a fine mist, the droplets of which fuse together when on the substrate), heat applications (where the paint has to be heated to get it fluid enough to be applied), radiation curing (where the coating is polymerised by high intensity ultra-violet or electron beam radiation) or two-pack systems (where an activator is added to a base coat for a limited pot-life paint). For the domestic market, the options are limited to brush or roller, and to ambient temperature.

2.1.5. Drying times

As with application methods, drying times can be different for factory or on site and domestic applications. A factory is able to apply heat (a process termed "stoving") or other means to accelerate the drying. Domestic requirements will typically be touch dry in under six hours, and through dry (a condition where the coating is completely solid from top to bottom) in sixteen hours at ambient temperatures. Waterborne paints have a minimum film forming temperature, below which they cannot form a coherent film.

2.1.6. Durability

Durability is not only used to describe resistance to weathering, but also the intended service life of the product. A wooden window will only suffer occasional abrasion, when cleaning, and opening the jamb. Wooden decking of a ship will suffer severe abrasion due to people walking on it on a constant basis.

2.1.7. Toxicity

Different components of a paint will have different toxicities, and different forms of the same component will again affect toxicity. Iron oxide is, in itself, non-toxic, but when in the form of a finely divided powder for use as a pigment in the paint making stage, it can be hazardous to health if the dust is not contained. Different solvents also have varying toxicities, generally aliphatic solvents (which dissolve fewer resins) are less toxic than aromatic solvents (which have a better "cut", i.e. they can dissolve more things, faster).

This means that a difference can be drawn between factory applied and domestic situations. A factory can use more toxic solvents, and coatings producing toxic by-products, or using toxic components, because a factory can equip its workers with safety equipment, and utilise extraction equipment for the safe neutralisation of the toxic components. Domestically applied coatings must utilise components with low toxicities as the manufacturers of the coating have no control over how their product is used.

2.1.8. Cost

The cost of painting the finished product is often more important than the individual paint cost. Factory applied products may use a coating which is more expensive in terms of £/litre, but is more economical to apply than a competitor's product, and thus an overall cost saving may result. Domestically applied coatings are priced can for can, although as with any other product, the consumer can buy different qualities of paint, and the final cost of the paint reflects the final market. A high quality "micro-porous" decorative paint for a front door will always be more expensive than creosote for a garden shed.

2.1.9. Specifications

There may be legal requirements for the formulation, for example, for use on a Grade 1 listed building. Customers may also specify a formulation parameter, for example, "lead-free" paint.

2.1.10. Special factors

Here other requirements have to be considered, for example, does the consumer require non-drip properties, ease of cleaning, especially low toxicity (e.g. for use on children's toys), etc.

2.2. Paint components

2.2.1. Resins

A resin is so called because early paints had to use naturally occurring resins, secreted by many plants, and especially fir and pine. When synthetic alternatives were developed, the name had become a paint term, and so the new compounds (which often differ markedly, in chemical terms, from their plant analogues) were still called resins.

The main purpose of the resin is to form a coherent film so that it can bind the pigment together, and adhere to the substrate. For this reason, a resin is also referred to as a “binder”.

We will consider two types of resin here, namely alkyds and acrylics. They each use a different type of solvent, white spirit for alkyds, and water for acrylics. In the domestic paint industry, a coating is termed “solvent borne” or “water borne” depending on whether the main volatile components present are organic solvents or water.

2.2.1.1. Alkyds

The name "alkyd" was first used by Kienle in 1927 for the polyester reaction products between polyhydric alcohols (AL from ALcohol) and polybasic acids (KYD, the phonetically modified end of aCID - alkyd sounding better than alcid)[6]. These early alkyds were hard, brittle and insoluble unless mono-basic fatty acids (usually introduced as a triglyceride oil) were incorporated into the reaction mix. The resulting product was termed an “oil modified alkyd”. In time, the description "oil modified" was dropped. However, later when a new generation of alkyds were developed (which could be used in the coatings industry), they were dubbed “oil free alkyds”, to differentiate them from the oil modified alkyds, and other types of polyester.

2.2.1.2. Acrylics

Acrylics derive their name from the plastics industry, using polymers of acrylic acid. They are also the generic term for polymers with similar chemistry e.g. methyl methacrylate and n-butyl acrylate. They are commonly prepared by a technique known as “emulsion polymerisation”. This not only uses reactants in the form of emulsions, but also commonly yields the product in this form. Their importance to the paint industry lies in the fact that they can form stable emulsions in water.

Emulsion polymerisation uses a technique which forms particle sizes between 0.005 and 5μm, and the initiator necessary for the polymerisation is soluble in water. This is the opposite to solution polymerisation, where the initiator is dissolved in the monomer[7].

In emulsion polymerisation, a long chain fatty acid salt is first dispersed, forming micelles with the hydrophobic tails in the centre (the like charges on the surface of the micelles repelling each other). As monomer is added, it migrates into the hydrophobic centre of the micelles, where the polymerisation reactions take place[7].

2.2.2. Pigments

The main properties required of a pigment are decoration and protection. The main pigment can be expensive, in which case diluting pigments, termed "extenders" are employed to reduce the cost of the paint. The pigments can be split into two main types, (1) opaque and (2) semi-transparent.

2.2.2.1. Opaque pigments

Opaque pigments are used when the surface has to be obliterated, for example to hide repair work, or to match an existing colour scheme. The opacity is achieved by a difference in refractive index between resin and pigment. Resins typically have a refractive index[6] of about 1.5. Pigments which appear white in the liquid paint have a refractive index of about 2 or greater (zinc oxide 1.99, rutile titanium dioxide 2.76 and anatase titanium dioxide 2.52)[6].

Extenders have a similar refractive index to liquid resins[6], about 1.5, but can appear white when the resin dries (in much the same way that common salt appears white due to microscratches on the surface). This is due[6] to air having a refractive index of 1.00. In order for this “dry hiding” to work, the extender must not be “wetted” by the binder.

White opaque paints tend to use the rutile form of titanium dioxide, which resists chalking better than the anatase form, although being slightly yellower[8]. Entwhistle[9] also notes that the high reflectivity of the rutile form renders it more opaque than the anatase form (and more opaque than other white pigments and extenders).

2.2.2.2. Semi-transparent pigments

Semi-transparent pigments are designed to allow the natural characteristics of the wood to be revealed by transmitting visible light, while scattering damaging UV radiation, and preventing it reaching the substrate. They can also be used to change subtly the appearance of the substrate, so that the new pine takes the appearance of antique pine, or even teak (if only in terms of colour). These pigments tend to be very finely divided versions of opaque pigments[8].

2.3. Paint making

There are a number of methods which can be used in the manufacture of paints, usually being batch (rather than continuous) processes[10]. These methods use

- Ball mills
- Attritors
- High-speed dispersers
- Sand mills
- Roll mills

Basically, the pigment is mixed with resin and a small amount of solvent, so that the viscosity is high enough to sustain the shear forces needed to disperse the pigment. The aim is to ensure that each pigment particle is coated with resin (a process known as "wetting"). This "millbase" (a term applied to the high viscosity paint before, during and after milling) is then "let down", i.e. diluted to the required viscosity.

2.3.1. Ball mills

Ball milling is a batch process using sealed drums partly filled with either spherical balls, cylinders or pebbles, and partly "charged" with the millbase. The drum is then rotated horizontally about the longitudinal axis, generally for between eight and thirty-six hours[8].

2.3.2. Attritors

Attritors differ from ball mills in that the cylinder is operated vertically, and is kept stationary. The grinding action is caused by balls being agitated by a rotating shaft fitted with bars or spokes. This process is about three times faster than ballmilling[7], and can handle higher viscosities, but requires greater supervision. This can be based on either batch, or continuous production.

2.3.3. High speed dispersers

High speed dispersion is a batch operation which is based on a shaft fitted with a disk with blades round its edge, and rotating at speeds of up to 2,000 rpm. This is dipped into the millbase contained in a stationary, open, vessel[11]. This process generates a lot of heat, which can be a problem with evaporation (for solvent borne paints), and resin stability (for water borne paints).

2.3.4. Sand mills

Sand milling is a continuous operation, but requires a batch mixed pigment and binder[10]. It is sometimes termed beadmilling, depending on the grinding medium[8]. The millbase is fed though the bottom of the mill, passes through horizontally rotating discs, or blades, and through a filter at the top, which retains the sand or beads.

2.3.5. Roll mills

Roll mills are typically used to make high viscosity products, and do not use a grinding medium. The dispersing action is generated by hollow cylinders (through which cooling water is passed), rotating in opposite directions. These generate very high shear forces, which disperse the pigment evenly, even after only two changes in rotational direction (produced by the favoured triple roll mill).

2.4. Resistance to exposure

All paints are made with a specific intended use. Paints in use will have a finite lifespan which is the period it takes for the paint film to degrade to an unacceptable degree. Some knowledge of this lifespan is obviously required, even before the paint is selected in preference to a competitors' product. There are a number of ways to assess paint failure, and paint life.

2.4.1. Paint failures

The obvious signs of degradation of a paint film are first loss of gloss, followed by erosion. As resin erodes, pigment particles are released, resulting in “chalking” (Figure 2.1). This is so called because the unbound pigment has the visual appearance of blackboard chalk, and any colours become whiter, again resembling blackboard chalk.

A paint is deemed to have failed when it ceases to perform its intended function. If a paint is required as an integral part of a architectural design, it will have failed if any of the defects below becomes unacceptable

- chalks (Figure 2.1)
- changes colour
- actively supports microbial growth
- becomes soiled or stained (Figure 2.2)
- blisters
- cracks (Figure 2.3)
- flakes

Figure 2.1. Chalking. Pigment loosened by erosion of the resin is transferred to the adhesive tape .

Figure 2.2. The sheltered part of the wall to the left has become soiled, but the paint is intact. On the right, the wall is not roofed. Rain has cleaned the black dust from the pointing, but the coating has failed .

The recognised function of a paint designed to protect wood, is to prolong the life of the wooden structure and, in many cases, to enhance the appearance. Any degradation that, for example, allows water to penetrate wood, or it to become blue stained (infected with, for example, *Aureobasidium pullulans* species) will rate a failure for the coating. A number of standards are used to assess the degree of failure[12,13,14,15,16], typically using a numbered scale.

If the paint is recoated before failure takes place, the lifetime of the coating may be prolonged indefinitely.

Figure 2.3. Cracking predominately along the grain and direction of brush strokes on this wooden house front door. If the coating had been sprayed onto a substrate with no grain, the cracking would tend to be hexagonal. Some accidental damage can be seen around the lock rose. This could account for the localised flaking.

2.4.2. Natural exposure

Natural exposure is the definitive way of testing the service life of coatings. Unfortunately, it is very protracted, a modern coating being expected to last at least five years before failure. Also, the location of exposure will affect the life of the coating, a panel exposed in a hot, humid, rain forest will perform differently from one exposed in an arid desert, or frozen tundra. Even apart from these extremes, "microclimates" will severely affect the life of a coating (Figure 2.2).

Even a few miles can bring significant changes in the physical effects influencing panel exposure. Coupled with this, the angle and aspect of exposure will affect the lifespan. An upright, south facing panel will stay drier longer than an almost flat panel facing north. In an attempt to rationalise these variables, the following factors should be specified[17]:

- Location (urban; industrial; marine; rural; or a mixed e.g. urban-rural)
- Height, angle and aspect of the exposure rack
- Nature of the terrain (e.g. concrete) above which the panel is placed
- Latitude

As a consequence of this, a common location is often stipulated, together with a common exposure angle (normally 45°), and aspect (usually toward the equator - i.e. South in the Northern Hemisphere)[17]. Florida is often used since the high level of solar radiation coupled with periodic heavy rainfall is a arduous environment for coatings.

Even with all these variables held constant, there is no control over natural variations from year to year. The best that can be hoped for is that, over the life of the coating, it will have experienced, on average, the same temperatures, rainfall, etc. as a previously applied panel.

2.4.3. Artificial weathering

In order to standardise the conditions that the coating experiences, a number of accelerated tests have been developed (e.g. enclosed carbon arc, QUV exposure, Xenon arc). While these tests are run to prescribed standards[18,19,20,21,22,23], they cannot reflect natural exposure very closely. This is because solar radiation cannot be exactly duplicated, nor can individual microclimates be adequately represented.

2.4.3.1. Carbon Arc Weatherometer[18]

For the Enclosed Carbon Arc, coated panels are placed around the interior of a drum which rotates on a vertical axis around a carbon arc lamp and a water spray jet. The drum revolves once every twenty minutes. A fan is mounted in the stationary drum cover, and can blow air into the drum to control the humidity and temperature of the panels. Over a twenty-four hour period, the nearly vertical panels are subjected to the following regime:

- four hours with the atomisers on and fan off - each panel will be wetted twelve times
- two hours with the atomisers off and the fan on - to dry the panels
- ten hours with the atomisers on and the fan off - this will simulate high humidity conditions, with the panels being wetted thirty times each
- two hours with the atomisers off and the fan on - to dry the panels
- five hours with the atomisers on and fan off - again this period will become very humid, the panels being wetted fifteen times each
- one hour with the instrument stopped, for maintenance and inspection of the panels

The carbon arc lamp is kept on for all periods except the maintenance and inspection hour. It is preferred that this test be kept running seven days a week, but there is no evidence that a shutdown over weekends and bank holidays affects the exposure, provided that the hours lost are made up to meet the required period of exposure. This test was specifically designed to duplicate, as far as possible, natural weathering in the UK. The types of paint which correlate best between the two types of exposure (natural/artificial), are oil-modified alkyds (synthetic resins made by condensing a polyhydric alcohol and a polybasic acid)[19] and oleoresinous paints (vegetable drying oils in combination with natural or synthetic resins)[19]. As a general guide, twelve weeks (2016 hours) of continuous exposure to this test should produce the same types of paint failure (in terms of loss of gloss, chalking, checking, cracking, flaking and water type blistering) as those occurring within three to four years of natural weathering in the UK, but colour changes are more difficult to predict.

2.4.3.2. QUV exposure[19]

QUV exposure is intended to simulate the degrading effect of water as rain or dew, and ultraviolet light. Panels are mounted almost vertically in front of UV fluorescent tubes.

There are three types of UV light

1. UV-A has wavelengths between 315 nm and 400 nm
2. UV-B has wavelengths between 280 nm and 315 nm
3. UV-C has wavelengths shorter than 280 nm

In the lamps used for this method, radiation is first generated by an electric arc through mercury vapour at low pressure. This radiation is absorbed by a phosphor which emits fresh radiation at a longer wavelength. The normal lamp for this test produces radiation in the range 280 to 370 nm but other lamps may be used.

Condensation is produced on the panels by having a well of heated water at the bottom of the test equipment. When the lamps are off, the panels cool and water vapour condenses on them. The water evaporates when the lamps are switched on and the chamber temperature rises.

Although a variety of UV and condensation conditions can be used, the following cycle is widely used:

- four hours UV at 60 °C
- four hours condensation at 50 °C
- eight hours UV at 60 °C
- four hours condensation at 50 °C

The 50 °C temperature is maintained by the heated water vapour. The extra 10 °C for the UV cycle is generated by the heating effect of the lamps.

The ASTM standard does not give any information about correlation between natural weathering and exposure in a QUV weatherometer[20].

2.4.3.3. Xenon-arc exposure[21]

British Standards do not record any correlation for painted panels exposed to xenon arc exposure, and natural exposure, although in individual cases, the degradation of specific polymers when exposed to xenon arc may be calibrated to a set number of years at a specific natural exposure site.

Panels are exposed to one or more xenon arc lamps fitted with filters to attempt to duplicate solar UV and visible light, or with different filters to represent sunlight filtered by 3 mm window glass.

There are four operating modes.

- continuous operation, wet and dry periods - Cycle A
- discontinuous operation, wet and dry periods - Cycle B
- continuous operation, no wet periods - Cycle C
- discontinuous operation, no wet periods - Cycle D

Cycles A and B are used for artificial weathering, C and D are intended to simulate conditions behind window glass.

For the wetting cycles, the panels are sprayed or totally immersed in water for eighteen minutes, before being dried under a relative humidity of between 60 and 80%. For the cycles C and D, which have no wet periods, the relative humidity is maintained at between 40 and 60%.

2.4.3.4. Salt spray[22]

Resistance to artificial seawater spray, as this test is described, is somewhat a misnomer, in that the spray is directed at a wall of the test cabinet, thereby forming a salt fog. The salt solution is made by dissolving the following weights of salts in distilled water to yield one litre of artificial seawater.

sodium chloride as NaCl	26.5 g
magnesium chloride as $MgCl_2$	2.4 g
magnesium sulphate as $MgSO_4$	3.3 g
potassium chloride as KCl	0.73 g
sodium hydrogen carbonate as $NaHCO_3$	0.20 g
sodium bromide as NaBr	0.28 g
calcium chloride as $CaCl_2$	1.1 g

The calcium chloride must be added in such a way that calcium carbonate is not precipitated. This can most easily be achieved by dissolving the first six salts in about 900 cm^3 water, and then adding the calcium chloride, either as an anhydrous salt powder, or as a solution in some of the remaining water and finally making up to the required volume.

Other salt spray tests use 5% w/w sodium chloride in distilled water sprayed at 35 °C; or a cycling wetting with salt fog, then drying, a technique termed prohesion. With prohesion, a British Standard has recently been adopted, but the process is used to describe exposure to a variety of salt fogs, and drying by compressed air at a variety of temperatures.

These methods test for blistering, softening, and rust staining (if applicable). There is no correlation between these tests and natural exposure cited in the standards.

2.4.3.5. Resistance to humidity[23]

In order to test particularly for resistance to humidity, painted panels are placed nearly vertical, and subjected to warm air at 100 % RH. The moist air cycles from 42 °C to 48 °C, and back to 42 °C in one hour by means of a heater in a water reservoir and the air chamber. The idea of this cycling is that as the humid air cools, it is forced to condense on the panels (and the walls of the cabinet). This tests for blistering and corrosion not induced by salt.

2.4.3.6. Sulphur dioxide exposure[24]

A sulphur dioxide exposure test will give an indication of how well coatings will withstand polluted atmospheres containing sulphurous acid. Correlation between exposure to this test to a period of natural weathering will be difficult owing to the intermittent concentration of sulphur dioxide in even the most polluted industrial areas.

Vertical panels are placed in a sealed chamber, with water in the bottom. A quantity of sulphur dioxide (at volumes at ambient temperature and pressure of either 200 cm^3, 1 litre, or 2 litres per cabinet volume of 300 litres) is introduced into the air space, and the water heated until the air temperature reaches 40 °C. This is maintained for eight hours, when the panels are exposed to clean air at 23 °C and 50 % RH for a further sixteen hours. This is one cycle. Panels are examined at the end of each cycle for blistering and corrosion. After the required number of cycles are completed, the panels are left for a further twenty-four hour period, when they can be examined for loss of adhesion, change of colour, and embrittlement.

2.4.3.7. Accelerated versus natural weathering

Correlations between each individual accelerated weathering test and natural exposure are poorly understood. Indeed in some instances no correlations can be established. This is accentuated by the variability between natural exposure sites.

Certainly, if accelerated weathering is used, a standard paint of similar composition should always be tested alongside the coating under evaluation[8]. This standard paint should have a well defined history of natural weathering. If the test coating fails before the standard, it is deemed to be an inferior product. If, however, the test coating is superior under accelerated weathering, there is no positive guarantee that a similar effect will be observed in service.

3. Wood as a substrate

Wood is, by its very nature, variable and thus suited to a variety of uses[24]. In order to understand the nature of wood, and the reasons for protecting it, it will be useful to consider, in simple terms, the structure and type of wood, and processes of degradation.

3.1. Structure

The properties of wood are dictated by both its microscopic and macroscopic structure. In a simplistic sense, the microstructure of wood is a porous material consisting of cells with hollow cavities, called[25] lumens.

On a macroscopic scale, it is helpful to group wood into two classes, the softwoods and the hardwoods. Softwood is from conifers and hardwoods from broadleafed trees. Conifers have needle shaped leaves and most are evergreen. The botanical division for softwoods is termed gymnosperms, and they have their seeds unprotected within cones. Hardwoods come from the division angiosperms, and most in temperate climates are deciduous. They have seeds contained within a fruit or nut.

Terming the woods softwood and hardwood is, perhaps, misleading, since some timber classed as hardwood (e.g. balsa) is softer than many softwoods (e.g. pitch pine and yew)[25], and some softwoods are harder than hardwoods[24]. For the majority of cases for structural timber, hardwoods are harder, and stronger than softwoods[26].

3.1.1. Softwoods

In softwoods there are two types of cells, trachied (for conduction and support) and parenchyma (for storage). The most common cells are trachied, and these are about 100 times longer than they are across. They have holes termed pits in the side walls, and these pits allow the flow of fluids. The alignment of these cells is along the main axis of the tree, giving the tree support. The parenchyma cells have a length to diameter ratio of about 7 to 1, and are mostly found horizontally, in the rays.

Wood formed early in the growing season has cells with thin walls and large lumens. Later in the growing season, wood is formed with thicker walls, and narrower lumens. These can be seen as alternating light and dark bands of the earlywood and latewood respectively. More importantly, water and other fluids are able to penetrate earlywood more than latewood due to the larger lumens, and this has a strong influence on the performance of wood coatings.

Another important feature of wood is the distinction between sapwood and heartwood. Sapwood is a layer of physiologically active wood[25], underneath the bark. The central core of the tree has no living cells and is called the heartwood. This stores food materials[25] which is converted into complex organic chemicals, which may alter the wood. The width of the sapwood remains relatively constant as the tree grows, and so the proportion of sapwood to heartwood decreases with increasing age of the tree.

Sapwood is permeable to water and other fluids, with the absolute permeability dependant on the species. Heartwood is generally impermeable, and often possesses a natural durability, arising from the chemicals stored there. Noble et al[27] found that for tangentially sawn Scots Pine, the absorption rate after one minute was 2098 $cm^3\ m^{-2}\ h^{-1}$ for sapwood, and only 233 $cm^3\ m^{-2}\ h^{-1}$ for heartwood.

Important softwoods in the construction industry include:

Scots Pine, also known as[26,28] European Redwood, (Pinus sylvestris);
Norway Spruce, also known as[26,28] European Whitewood, (Picea abies);
Douglas fir (Pseudotsuga menziesii);
Western red cedar (Thurja Plicata).

Scots Pine was used in this study. Its qualities depend largely on the location in which it is grown; the slow growth from northern areas is considered to produce better timber for joinery. It has[24] a good strength to weight ratio, is easy to work, and has a low cost[26]. Its disadvantages[24] are that it can be resinous, and often contains large knots.

Spruce also has a low price, and good availability, but is often not used for joinery due to difficulties in preserving and machining it. Douglas fir has better working qualities than Scots pine[26] and is available in long clear lengths[24,26], but at a higher cost[26]. Western red cedar also has good working qualities[26], but its low strength limits its use[24].

3.1.2. Hardwoods

On a microscopic scale, hardwoods have four types of cells: fibres (for support); vessels or pores (for conduction); tracheid (for conduction and support); and parenchyma (for storage). Tracheid cells are fairly uncommon in hardwoods. Instead, they rely on vessels for conduction, and in these cells, the end walls are partly open, allowing conduction of water and other fluids. Hardwoods rely on fibres rather than trachied cells for support; fibres have the same length/diameter ratio (100:1) as trachied cells, but do not have pits, and so do not allow the conduction of fluids.

As with softwoods, hardwoods growing in temperate climates will show growth rings as earlywood and latewood, but those growing in climates where seasonal variation is less marked may have more uniform growth. As described above, the proportion of sapwood in the tree will decrease with time.

Important hardwoods for the construction industry include:

Iroko (Chlolophora excelsa);
Oak (Quercus robur);
Sapele (Entandrophagma cylindricum);
Teak (Tectona grandis).

All of the above hardwoods are more durable[26] than the softwoods listed above, but the relative price can be higher, and the wood may not be so readily available. Not all hardwoods are more durable than softwoods - ash (Fraxinus excelsior) and beech (Fagus slyvatica) for example are perishable[24].

3.2. Molecular structure and chemistry

Wood is physically, chemically, and morphologically a complex and heterogeneous material, varying in its properties according to species[29], growing situation[30] and also the physical location in the tree[29].

Chemically the major constituent of wood[29] is cellulose, which accounts for 40-50% w/w. Cellulose chains occur in microfibrils, some regions of which are aligned and crystalline in nature, whereas the remaining amorphous regions are highly hydroscopic.

Cellulose components are embedded in a matrix made from hemicellulose and lignin. Hemicelluloses are carbohydrates but have lower molecular weights than cellulose and form about 20-25% w/w of the wood. Together, cellulose and hemicelluloses are termed holocellulose. Lignin is a phenyl propene polymer of variable molecular weight and also forms about 20-25% of the wood's mass. These cellulosic and lignin components are bound in a complex physical and chemical matrix termed[24] lignocellulose.

The lignocellulose complex is largely inert to coatings, but wood also contains typically[30] 5%, but up to[24] 10% of extractives, which can be highly reactive. The extractives can include[24,30] fatty acids, lignan, stilbenes, tannins, and terpenes. Fatty acids should not cause a problem to coatings. Lignans should not be confused with lignin, as they have a very different chemical composition. They are[24] water soluble polyphenoids and highly acidic; they can cause staining in coatings. Stilbenes are yellow, turning to brown when oxidised, and can degrade coatings[24] by migration from knots. Tannins[24] are water soluble polyphenolic compounds, and cause discolouration round nail holes. Terpenes[31] are unsaturated highly reactive compounds with empirical formulas $C_{10}H_{16}$, $C_{15}H_{24}$, and $C_{20}H_{32}$. These are responsible for many of the odours from wood.

3.3. Moisture in timber

A newly felled tree usually contains a greater weight of water than it does of wood[24]. Much of this water is contained in the lumens; as this water is lost, no dimensional changes occur. Eventually, all the lumens will be empty, but the cell walls will be saturated. This is known as the fibre saturation point, and is when the timber has approximately 30% of water. Timber has to be dried further before use.

Drying below the fibre saturation point results in shrinkage. Shrinkage is used to describe the dimensional changes from “green” to seasoned timber, any subsequent dimensional changes is referred to as movement. Shrinkage is not uniform over the timber: for Scots pine, drying from “green” to about 12% moisture content results[24] in 4.5% tangential, 3.0% radial and less than 0.1% longitudinal shrinkage. Other species will have different shrinkage ratios, for example, for beech (Fagus sylvatica) the shrinkage is 9.5% tangential, 4.5% radial and less than 0.1% longitudinal.

Although there is very little movement and shrinkage in the longitudinal direction, the majority of water ingress is through the longitudinal face. The transverse ("end grain") surface has a much higher permeability; for Scots Pine sapwood 21,283 cm^3 m^{-2} h^{-1}, and for heartwood 4723 cm^3 m^{-2} h^{-1}, both values determined after one minute of exposure. Miller and Boxall[32] found that when Scots Pine heartwood end grain was exposed to moisture, it was essentially dry 3 cm from the wetted end, conversely the sapwood had a moisture content greater than 30% 9 cm from the wetted end after 24 hours.

3.4. Mechanisms of deterioration of wood

3.4.1. Moisture

Water ingress can be the most damaging factor in deterioration of wood. The different degree of movement in the radial and tangential dimensions can result in the timber warping and bowing. In extreme cases, due to poor design, timber can tear loose from its fixings due to movement[24]. If, for example, a window jams as a result of movement, efforts to free it can loosen mastic and joints[24], causing greater water uptake. Additionally, rapid changes in moisture content (caused by either a porous coating or untreated timber) will lead to splitting of the timber[33].

Apart from physical damage caused by water, related coating defects can occur[24]. Wet wood can cause poor coating adhesion, by plasticising the coating, and by migration of water soluble material to the wood/coating interface. If high vapour pressure occurs in coated wet wood, for example by sunshine (especially on dark coatings), blisters can form. Flaking can occur by either loss of adhesion, or by rupture of a blister.

Moisture can also act synergistically with other sources of deterioration. A classic example of this is that colonisation of wood by microorganisms cannot occur below a specific water content (20% for dry rot).

3.4.2. Biological attack

Biological attack can be split into two distinct sections, fungal attack and insect damage. Both types are very dependant on the condition of the wood: fungal attack requires a minimum moisture content in the timber, and insects will also only colonise under favourable conditions.

3.4.2.1. Fungal Attack

The ability of micro-organisms to utilise timber is well documented[24,34]. If the timber has less than about 20% w/w water, it is resistant to fungi such as dry rot[25,35]. Paradoxically, this can mean that painting can cause the early failure of a wooden structure. If, for example, there is a crack along a join, or a flaking paint film, water can "wick" along the surface of the wood. It can then be sheltered from sun and wind which would cause the water to evaporate. The wood can absorb the water, allowing the percentage of water in the wood to rise, allowing wet rot to colonise the wood (Figure 3.3.2.1).

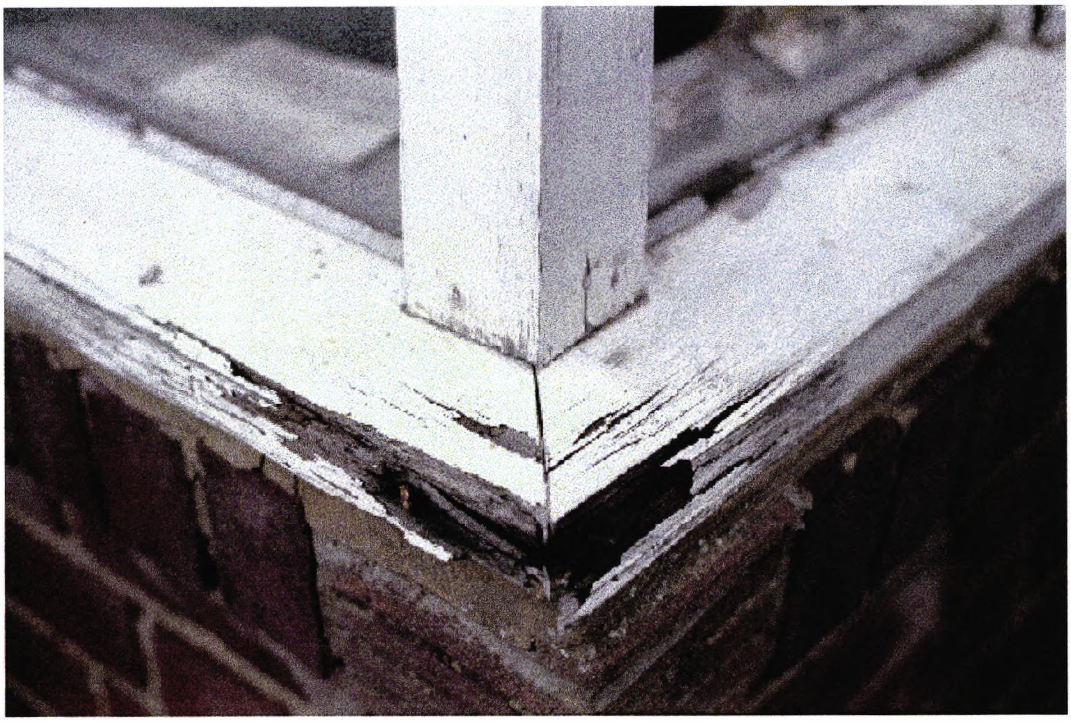


Figure 3.4.2.1. By poor design and by poor maintenance, water has entered the wood through the transverse face exposed by the butt joint, and has been retained by the coating, causing rot to set in.

3.4.2.2. Insect damage

In the UK, unpainted constructional timber is most likely to be attacked by the common furniture beetle (Anobiidae), commonly referred to as woodworm. Unless the infestation is especially severe, structural integrity is not compromised[24]. A more serious, but more regional effect is from longhorn beetles (Cerambycidae)[28] which is prevalent especially in certain parts of the south east of England. Longhorn beetle larvae can live up to ten years[24] and so severe structural damage can occur.

3.4.3. Photodegradation

All woods exposed to the weather experience a progressive loss in colour and surface erosion under the action of sunlight and rain. In time the surface is converted to an unsightly layer of loosely attached degraded wood fibres. In a clean environment this may be an attractive silvery grey colour, but more usually it is rendered unsightly by an accumulation of blue stain fungae and dirt.

As the rate of loss of wood material is relatively slow at about 5 mm per century, photodegradation has few implications for the structural performance of exposed wood, but it is of major significance from the standing of coatings performance. The most serious problem is lack of adhesion - the coating is easily detached with the degraded wood fibres. This statement is true for both new paint on weathered wood, and for coatings that allow photodegradation of the wood surface (e.g. transparent varnishes). Prior to maintenance painting, wood that has been exposed for two weeks or more has to be sanded back to fresh wood[4]. Even if such preparation is carried out, Boxall and Smith[5] found that the coating is more likely to fail than if the coating was applied to new wood.

Another problem, if transparent coatings are to be used, is colour changes. Desch[34] reports that colour changes in wood depend on exposure to light and air, as well as heat, and that the type of light can bring about different colour changes, for example, mahogany fades under strong sunlight, but darkens in moderate light.

Considerable research into the photodegradation of wood has been carried out in recent years. General findings are that both visible and UV light are known to have a severe effect on wood[36-42]. Derbyshire and Miller[38] placed wood strips in cells fitted with filters to allow exposure to light of different wavelengths. They found that both UV and visible light were significant in the photodegradation of wood.

Certainly UV is usually acknowledged[40,41] to have the most damaging effect, but short wavelength UV is only a small proportion of visible light[43], and so both UV and visible photodegradation must be significant. Hon[44] and Chang[45] found that UV radiation can only penetrate 75-80 μm, whereas visible light can penetrate 200 μm, and this increased depth of penetration increases the effect of visible light photodegradation on the mechanical strength of wood.

Lignin is more susceptible to photodegradation than cellulose[46,47]. Derbyshire et al studied the mechanical strength of unweathered and weathered wood, and found[46] that in unweathered wood, failure was initiated by weak points in the latewood, with the crack propagating in stepwise fashion in a direction perpendicular to the applied load. In latewood, the crack surface was smooth, and in earlywood it was rough. In the early stages of weathering, lignin degradation allowed a more brittle type of failure, with the crack surface of the earlywood becoming smooth. As weathering advanced, cellulose breakdown led to failure in interfiber breakdown, resulting in a 60% loss in strength.

3.5. Protection of wood

3.5.1. General

In almost all applications of wood out of doors the performance of the component is strongly dependent on effective protective from some form of surface coating. The principle function of the coating is to prevent penetration of moisture, which will otherwise result in dimensional movement, splitting and distortion, and also introduce a risk of decay. The coating also serves to protect the surface of the wood against photodegradation by sunlight.

It is now generally accepted that for jointed components in particular, it is not prudent to place total reliance on the abilities of a surface coating to provide a barrier against water entry, and that a second line of defence in the form of preservative treatment is necessary.

3.5.2. Control of moisture content by coatings

Intense development effort in the coatings industry has resulted in a very wide variety of natural and opaque wood coatings, based on solvent borne and water borne resins. For present purposes three main types will be distinguished, namely varnishes, exterior wood stains, and opaque paints.

Varnishes[48] are transparent coatings with little or no pigmentation. If they contain UV absorbers they may be suitable for exterior use, but mostly they are only suited for interior use. These coatings may allow photodegradation of the wood surface, resulting in early failure due to poor adhesion at the degraded wood/sound wood interface.

Exterior wood stains are varnishes with some pigmentation. This pigmentation is usually very finely divided, so as to allow the majority of visible light to pass through, whilst absorbing UV. Some colour is usually imparted to the wood, but the grain structure is preserved.

Opaque paints attempt to block all radiation from hitting the wood surface. They can have 60% w/w pigment, but for exterior use all of the pigment must be “wetted” by the resin. These paints are used where the wood is a convenient building material, but also where a different colour scheme is desired.

Each of these types can be formulated to have a specific permeability[49]. Falla[50] found that for maximum durability of the coating, the water permeability should not exceed 3.5 mg cm^{-2} day^{-1}. In practice, the actual permeability will depend on the application, in terms of the permitted dimensional movement of the wood. This is generally placed into three end-use categories[51,52]: non-stable; semi-stable; and stable.

The non-stable category is where free movement is permitted (i.e. permeability is high). This category describes coatings for overlapping cladding, fencing and garden sheds.

Semi-stable is where some movement is permitted, for example in tongue and groove cladding, garden furniture, wooden houses and chalets.

Stable is where the minimum movement possible is required, such as in joinery, including windows and doors.

4. Coatings for wood

In order to investigate causes of degradation of paints, an understanding of the nature of paints, including additives is important. Paints in general were described briefly in Chapter 2. A more detailed review of the chemical nature of coatings specifically designed to protect wood is given below, and the review has been sub-divided into the resin classes, namely those resins which require a non-aqueous solvent (solvent borne coatings), resins capable of being dispersed in water (water borne coatings), and resins formed by hybridising the solvent and water borne resins enabling the hybrid to be dispersed in water (hybrid coatings).

4.1. Solvent borne coatings

Many vegetable oils are capable of reacting with atmospheric oxygen, by a free radical polymerisation mechanism, to form a three dimensional more or less solid structure. Catalysts reduce the time for this structure to develop.

Historically, paint was made using linseed oil and white lead pigment ($PbCO_3$). Free acid groups in the linseed oil reacted with the pigment and dissolved some of the lead. This then catalysed the cross-linking reactions in the oil. The replacement of the lead carbonate with other pigments necessitated the addition of other cross-linking agents, but linseed oil was still favoured for its supreme drying properties (i.e. its ability to form crosslinks). Linseed oil is capable of self autoxidation at the surface. Other metal compounds, traditionally containing lead were used to confer "through drying" (a process where the bulk crosslinks at a similar rate as the surface). Zirconium driers are now used, usually with calcium, in place of lead[53,54,55] in the light of health concerns.

These crosslinking agents are usually certain metals in the form of soaps, termed "driers". While these driers may be changed by the reaction process, their low concentration (they are usually present in fractions of a percent of the crosslinking matrix weight) and their influence on the rate of crosslinking means that driers are termed catalysts.

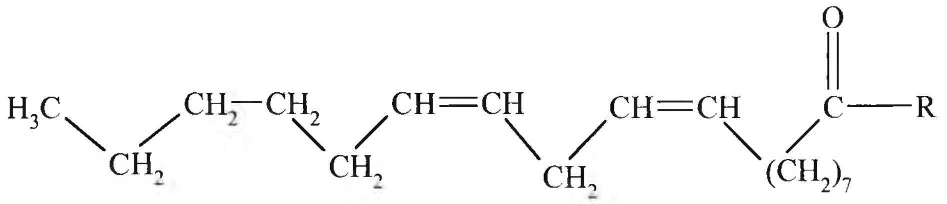
With the development of better driers than lead carbonate, other oils, both naturally occurring and synthetic blends, can and are used, depending on their relative price and qualities imparted to the final coating.

4.1.1. Alkyds

The alkyds used in this study are, in simple terms, polyesters with an air drying component. Alkyds in general are usually solvent borne (typically with white spirit, or less commonly xylene), but are sometimes synthesised to be water borne. BS 2015 describes alkyds as synthetic resins, made by condensation between a polyol and a polybasic acid, often with a vegetable oil and/or other modifications[48].

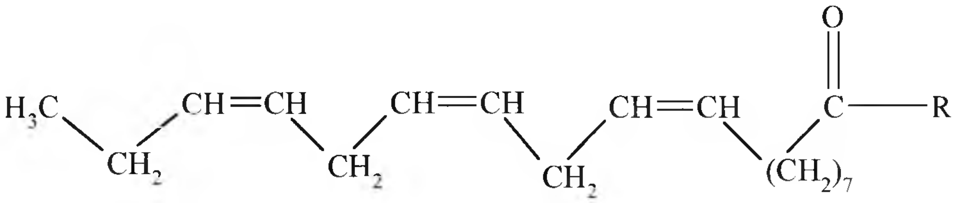
4.1.1.1. Synthesis

The air drying nature of alkyd resins is imparted by incorporating unsaturated vegetable oils when the alkyds are made. The most important unsaturated esters are those which contain linoleate and linolenate groups. Linseed oil is a triglyceride which contains approximately 60% linoleate and 25% linolenate groups.



Linoleate.

R can be glycerol for the esters, or OH for the fatty acid.



Linolenate.

R can be glycerol for the esters, or OH for the fatty acid.

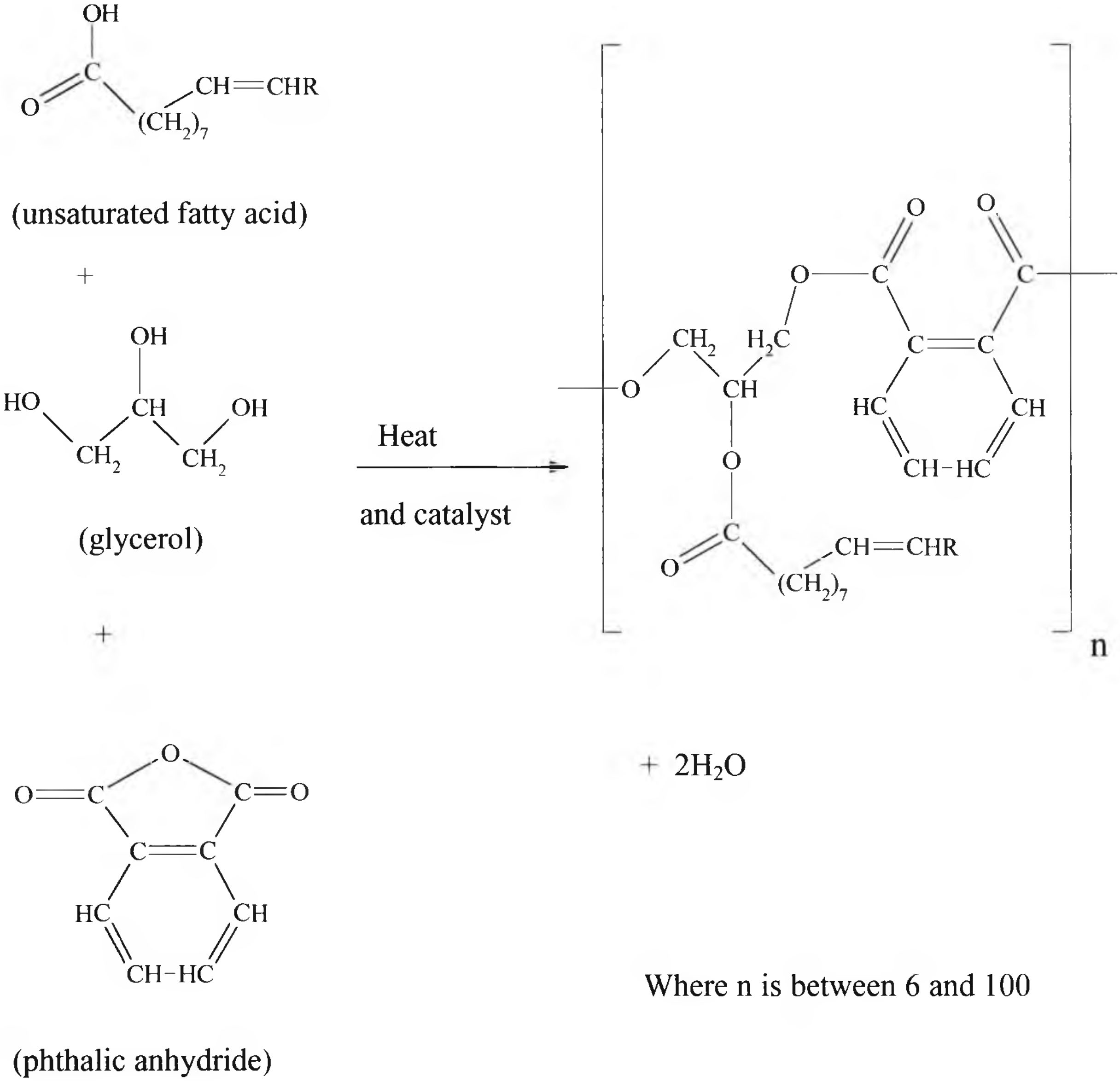
Generally speaking alkyds are made by heating together

1. a polybasic anhydride or acid (e.g. phthalic anhydride),
2. a polyol (e.g. neopentylene glycol or glycerol),
3. a triglyceride oil, traditionally linseed oil (or a fatty acid)

This condensation reaction forms a complex polyester, a process known as "cooking", and the reaction vessel is termed a "kettle". The complex polyester formed arises not only between the polyol and the anhydride (or acid), but also, due to transesterification, between the polyol and the triglyceride monobasic fatty acids, (which are formed when the triglyceride oil is partially hydrolysed and de-esterifies).

Modifiers such as styrene, rosin, and urethane are often added to the mixture. These modifiers, the cooking process, and the order of addition all make profound changes to the properties of the final coating.

Roff and Scott[56] describe three ways of preparing alkyds, all by a batch process. The first describes heating all the components together at between 200 and 280 °C. The reaction below is an example.



Where n is between 6 and 100

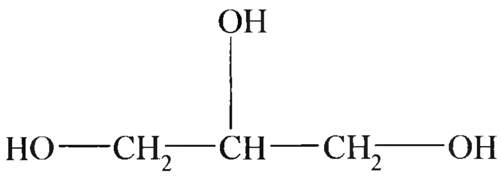
The second method is to react only the oil or fatty acid with the polyol first, to leave one or more hydroxyl groups, and then, in a second stage, reacting that ester with the polybasic acid.

The third method involves dilution of a polyol/polyacid polyester with a vegetable oil at high temperature.

4.1.1.2. Polyfunctional components

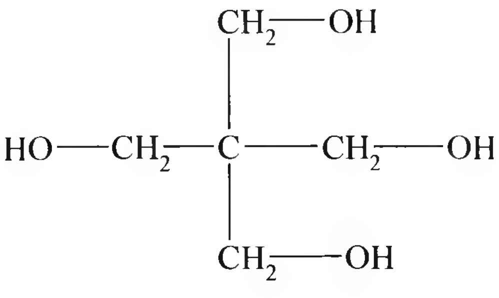
The anhydride used is commonly *o*-phthalic anhydride. This is readily available; has a good stability (due to the benzene ring); and is relatively non-toxic.

Acids with a higher functionality are not used due to lack of availability (and cost), and typically the three dimensional cross linked structure is formed from the polyol. Two components with polyfunctionality would give rise to crosslinking problems, possibly leading to solubility problems. Typically the polyol is either glycerol, pentaerythritol or neopentyl glycol (which would not contribute to a three dimensional structure). Glycerol will always be present if a trigyceride vegetable oil has been used.



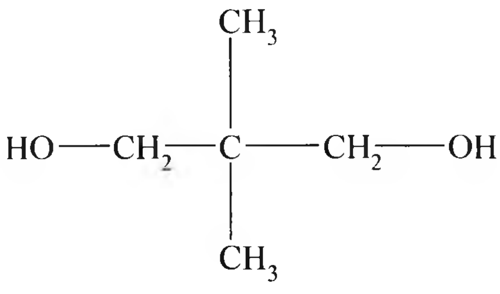
$$HO{-}CH_2{-}\overset{\overset{\displaystyle OH}{|}}{CH}{-}CH_2{-}OH$$

glycerol



$$HO-CH_2-\underset{\displaystyle CH_2-OH}{\overset{\displaystyle CH_2-OH}{C}}-CH_2-OH$$

pentaerythritol



$$HO-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH_2-OH$$

neopentyl glycol

4.1.1.3. Air drying component

The weight percentage of oil in the total resin is known as the “length”, and can be varied to adjust the drying properties of the coating. A short oil alkyd is one where there is a relatively small portion of oil to other components, and has the characteristics of very quick touch-dry times (a few minutes). Long oil alkyds, with a higher proportion of oil, are typically used as protective coatings for wood since they can be overcoated typically within twenty-four hours, and for the properties imparted by the high proportion of an air-drying crosslinked network. The difference in the drying times can be explained by the fact that the short oil alkyds contain more polyester than fatty acid, thus they dry predominantly by the loss of solvent. As the fatty esters are more dilute (and “locked” in place before autoxidation is complete), crosslinks between them are harder to form; with long oil alkyds, the converse is true.

The active parts of the oil are the linoleate and linolenate parts of the triglyceride, and these undergo autoxidation, a radical reaction, when exposed to oxygen. This is catalysed by, among other things, metals in the form of soaps, for example, cobalt octanoate. The reactions that cobalt driers promote was reviewed by Falla et al[53].

Cobalt soap is recognised as being a primary drier because it can be used alone. It tends to dry the surface before the bulk. As the resin crosslinks, it shrinks, partly due to the loss of volatile autoxidation products. If the surface crosslinks before the bulk, the surface will be drawn into ripples, known as “rivelling”, as the bulk crosslinks and shrinks. Cobalt driers are also very highly coloured (Figure 4.1), which limits the concentration that can be incorporated into a paint. Auxiliary metals are used to promote “through drying” (where the bulk of the film dries at a similar rate to the surface), drying under adverse conditions, etc. and these are now usually zirconium and calcium. Zirconium is generally considered to be more active than calcium and so the concentrations of the drier metals are listed in the order cobalt, zirconium and finally calcium. The exact role of each drier was studied by Falla et al[53,54,55].

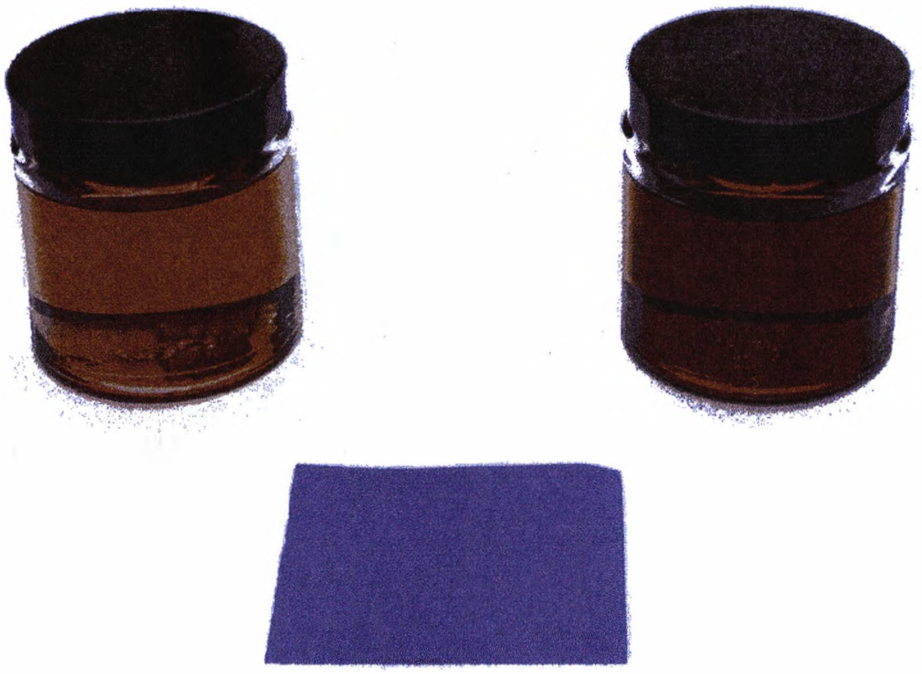


Figure 4.1. A long oil alkyd without driers on the left, and with 0.05% w/w cobalt on the right. Even a small deepening in colour can have a significant effect, especially for white and pale coloured paints. The purple square is the colour of a piece of white paper moistened with cobalt drier solution, and allowed to dry. It was placed on identical paper, which forms the background to the photograph.

The concentration of drier metal in paint with no solvent, nor pigment can be calculated from:

$$pd = (100.wd.pm)/(wr.NV)$$

where

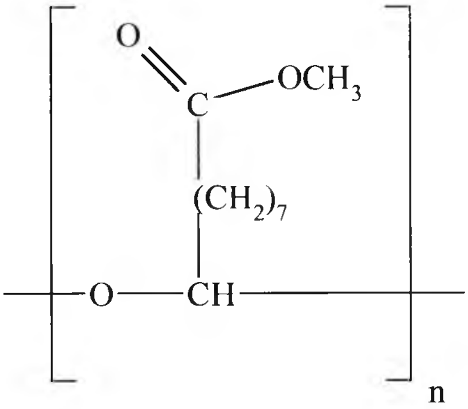
pd is the percentage of drier metal in the paint
wd is the weight of the drier solution added
pm is the percentage of drier metal in the drier solution
wr is the weight of the resin solution
NV is the weight percentage of non-volatile cross-linking resin, in its solvent

Thus, to make the varnish depicted in Figure 4.1, 0.3 g of a cobalt soap solution in white spirit (having a concentration of cobalt in the solution, pm, of 10% w/w) was added to 78 g of a long oil alkyd resin, having a non-volatile content of 76.2%, and so the percentage of cobalt (pd) is:

pd = (100x0.3x10)/(78x76.2) = 300/59436 = 0.05%.

4.1.1.4. Structure

The structure of dried alkyds has never been fully elucidated, but the air-drying autoxidation reactions have long been associated with the unsaturated part of the triglyceride oil, and cobalt is known to catalyse this radical reaction. In his work with methyl linoleate dried with cobalt, Falla[53] found that the polymer chain was probably formed of the following structure:



with terminal groups including -OH, -COOH and -CHO.

This ether could be joined to the polyester component if the OCH_3 group was replaced by OR where R is the polyester.

4.2. Water borne coatings

Water borne coatings are oil in water emulsions. A suspension of fine particles in water has a viscosity similar to that of water (Figure 4.2). As the viscosity of water (about 0.001 N m^{-2} s or 0.01 Poise)[57] is far too low to be usable as a paint, various thickeners must be added. The viscosity of the paints in this study was 3 to 4 Poise.

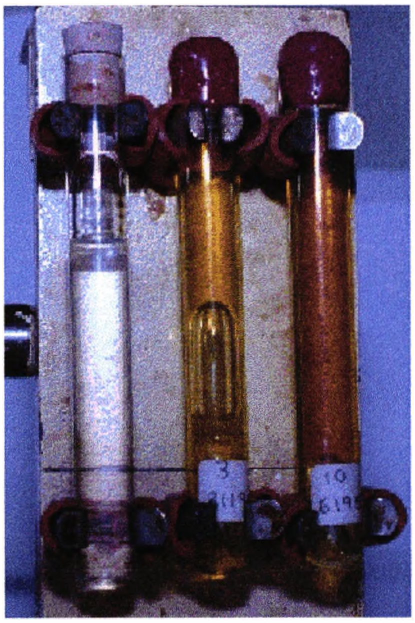


Figure 4.2. Comparison of viscosity using PRA standard bubble viscometers. Water is in the tube on the left, a one poise oil in the middle, and a five poise oil on the right. The bubble has reached the top of the water, which is clearly much thinner than the one poise oil, where the bubble is about half-way up the tube. The bubble for the five poise oil has yet to start to rise, and is just visible behind the tube label.

4.2.1. Thickeners generally

Oil in water emulsions do not have sufficient viscosity to be used independently as paints (Section 4.2.). In order to adjust the viscosity of the paint, thickeners must be used which either increase the viscosity of the aqueous phase, or bond to resin and pigment particles, developing a two or three dimensional structure. Those thickeners which bond to resin and pigment particles are termed associative thickeners. Some thickeners will cause an immediate viscosity increase, while others require certain conditions (e.g. pH adjustment) before viscosity changes, and/or associations form.

As the resin is hydrophobic, any groups on the thickener molecule which are to associate with the resin must also be hydrophobic. The thickener must also have a hydrophilic component so that it can interact with the aqueous phase, thus it is often a water soluble polymer chain. When associations with resin and pigment are reported in the literature, it is convenient to represent the hydrophilic polymer chain as a line, and the hydrophobic site of association as dots[58,59,60]. This notation must not be confused with that used for surfactants, where a small, hydrophilic, group is depicted by a dot, and the long, hydrophobic polymer chain as a tail[7,61,62].

There are four classes of thickeners, each with their own unique characteristics, which are detailed, in turn, below. The four types are:

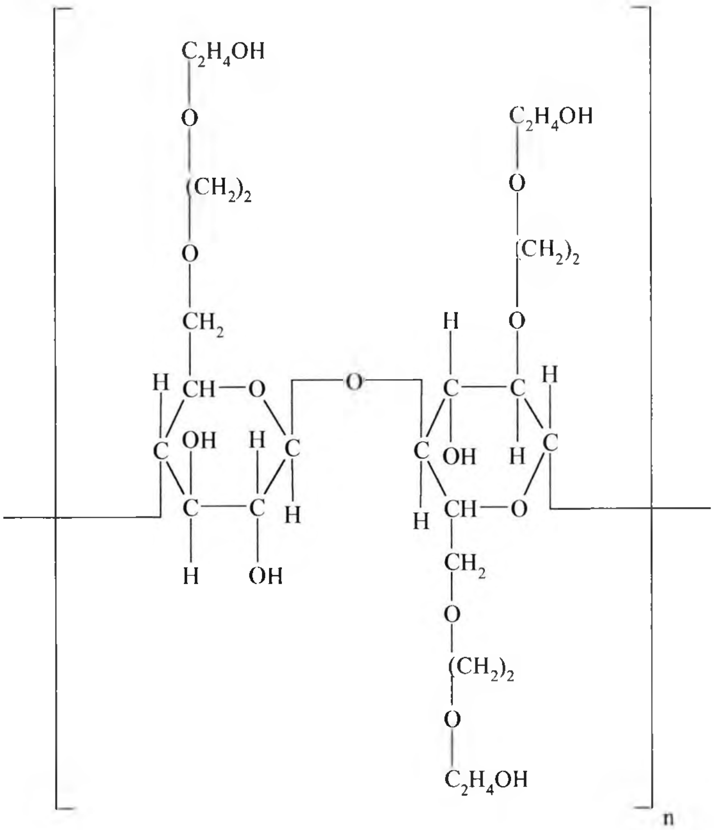
- cellulosic thickeners
- alkali soluble/swellable emulsions
- urethane thickeners
- acrylic/urethane thickeners

Cellulosic and urethane thickeners were used in this study, and so will be described in detail, the other two types were not used, and so will only be referred to briefly.

4.2.1.1. Cellulosic thickeners

Cellulose thickeners were the first to be developed, and the most common are hydroxyethyl cellulose (HEC) and hydroxypropyl methyl cellulose (HPMC)[59,63,64]. These are typically used at 5% of the liquid paint[65].

An idealised structure of hydroxyethyl cellulose is shown below.



idealised Fischer diagram of hydroxyethyl cellulose

The chain length is not disclosed for competitive reasons, as the size will affect the properties, but the dextran equivalent molecular size ranges[65] from 1,500,000 to 2,700,000.

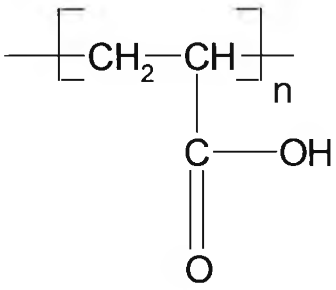
Cellulosic thickeners are very susceptible to microbiological attack[65], particularly by enzymes formed by micro-organisms. If one of the raw materials is contaminated by micro-organisms, addition of a biocide, which kills only the micro-organisms, will leave their enzymes unaffected. These enzymes may still destroy the thickener, significantly reducing the viscosity of the paint.

Cellulose thickeners dissolve in the aqueous medium, and are not attracted to, nor bonded to, any of the paint components. They increase viscosity at low shear rate, but readily shear thin (i.e. viscosity is reduced when a force is applied), and so spatter resistance (a key requirement for, in particular, those paints to be applied by roller) is poor. Additionally, levelling can be poor[59,63].

These limitations can be overcome, at least partially, by modifying the cellulose structure with hydrophobic groups. These new compounds are termed hydrophobe modified cellulosics (HMC)[59] and are now associative thickeners. Shay, Bassett and Rex[59] compared hydroxyethyl cellulose (HEC) with hydrophobe modified HEC (abbreviated to HMHEC[59], hmHEC[66], or HHEC[59]), and found that the associations increased brushing (high shear) viscosity as well as improving spatter resistance, sag resistance and levelling (where shear rates are low).

4.2.1.2. Alkali soluble/swellable emulsions as thickeners

Alkali soluble and alkali swellable emulsions (ASE) are polymer chains (typically polyacrylic acids[63,66]) with carboxylic acid groups[63] along the length. These form small micelles at low (typically 2.7 to 3.2)[67] pH. When the pH is raised (typically to 8 or 10 by the addition of ammonium hydroxide)[63], hydrophilic salts are produced which cause the polymer to uncurl and become soluble or swellable in water. This causes a viscosity increase[59,63].



Polyacrylic acid

The properties of this type of thickener can be adjusted by changing both the cross-linking and the molecular weight of the polymer chain[63]. The molecular weight typically ranges[64] from 10,000 to 100,000.

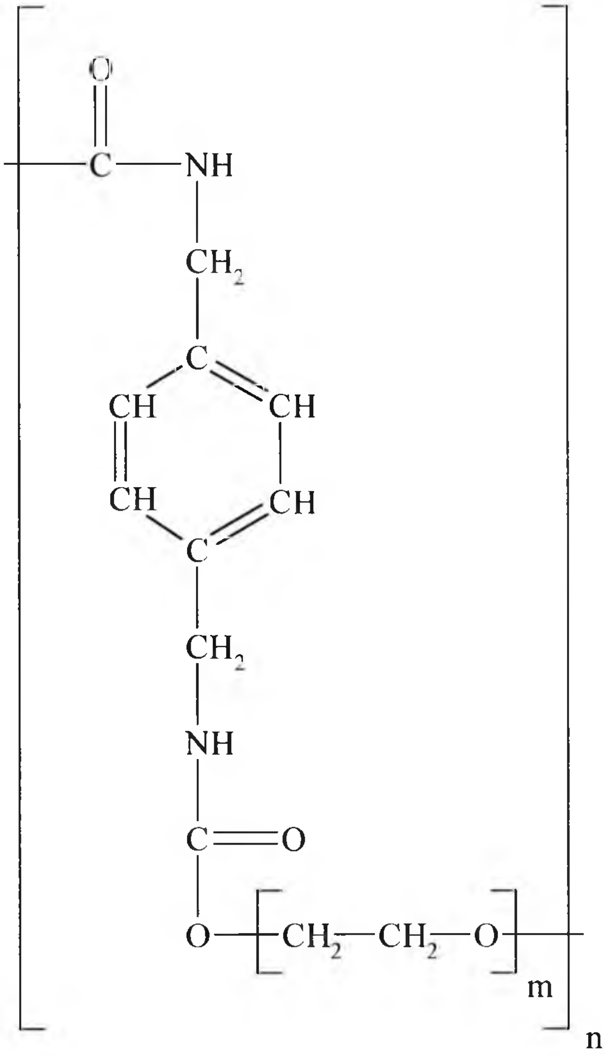
As with cellulosic thickeners, ASE can be made to associate with the resin and pigment by hydrophobic modification. These thickeners are termed hydrophobic modified alkali soluble/swellable emulsions (HASE)[58,60,63,67] or alkali soluble associative thickeners[63].

4.2.1.3. Urethane thickeners

Polyurethane thickeners are associative thickeners (Section 4.2.1.1.). They are termed hydrophobically modified ethylene urethane oxide rheology modifiers (HEUR)[58,64,67]. Molecular weights[58] are of the order of 40,000 to 50,000. The centre of the chain is hydrophilic, and the two ends are non-ionic hydrophobic groups.

The rheology of these thickeners is more Newtonian than cellulosic or acrylic (ASE) thickeners. They impart good flow and levelling properties[58,63], although they tend to shear thin and therefore have little effect on the high shear end of the rheological profile[68].

An example of the structure of a typical urethane thickener is shown below.

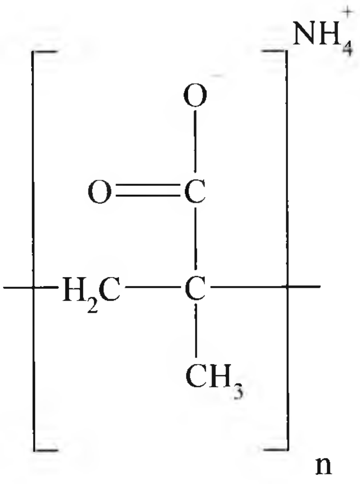


An example of a urethane thickener.

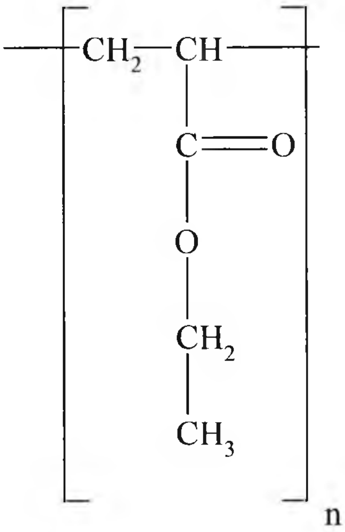
m is typically 50 and n typically is between 15 and 25.

4.2.1.4. Acrylic/urethane hybrids as thickeners

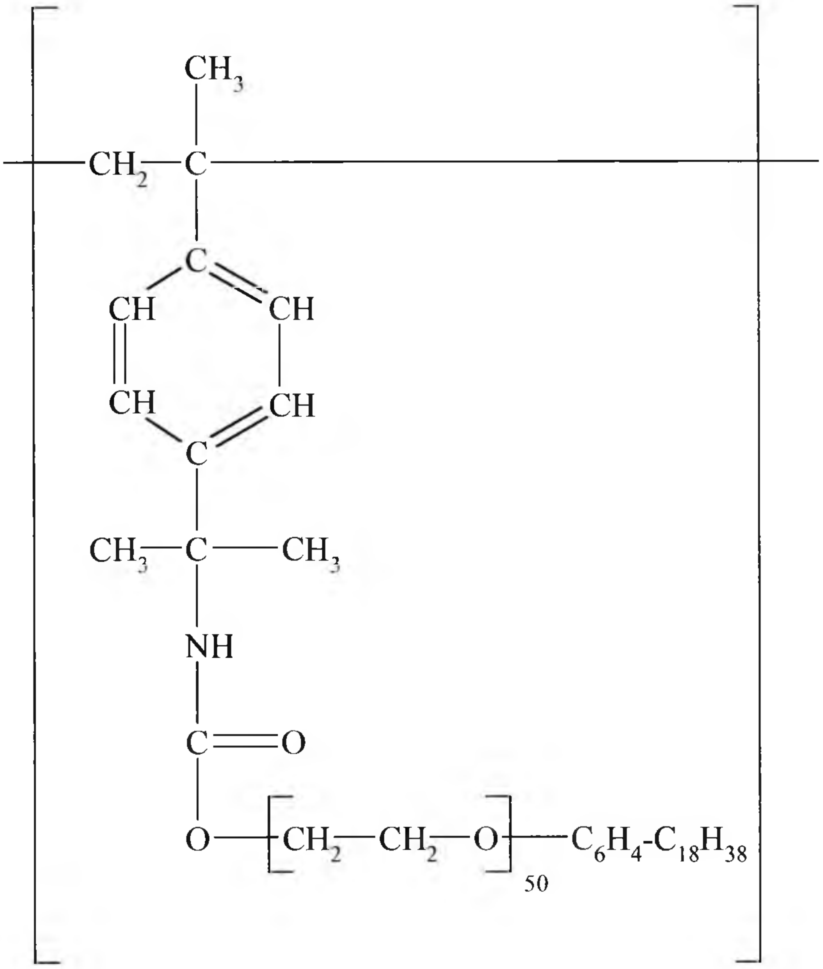
In order to overcome limitations of ASE and HEUR thickeners, a new type of thickener has been developed. This is a hydrophobically modified ethoxylate urethane alkali soluble/swellable emulsion (HEURASE). Unlike HEUR thickeners, these are anionic[60]. HEURASE thickeners incorporate the following three structures (although in which order and proportion is not revealed for commercial reasons):



Ammonium methacrylate



Ethyl acrylate



Urethane associative linkage

4.2.2. Dispersing agents

Powders such as pigments and extenders have to be dispersed into a liquid in order to make a paint. Traditional long oil alkyd resins are known to be better at “wetting” pigments than many modern polymers[68], and this facilitates dispersion. Pigments and extenders do not form stable dispersions in water, without a dispersing agent. In order to understand how dispersing agents work, we must first consider the particulate nature of the pigments and extenders.

When the pigments and extenders are made by the raw material manufacturer, they are small particles (usually crystals) which are termed[68] "primary particles". Even hydrophobic powders, however, adsorb water and form agglomerates. These aggregates, when in edge to edge or point to point contact, are called[68] "secondary particles". These secondary particles can be separated by dispersing agents. Occasionally, a crystal face meets another face, allowing chemical bonds to form between the two crystals, forming "tertiary particles", which can only be separated using the sort of forces that will break crystal structures[68].

Dispersing agents separate secondary particles by using electrostatic and/or steric forces. Six classes of dispersing or wetting agents are recognised[68,69], and are as follows:

- anionic dispersants (e.g. ammonium salts of fatty acids)
- cationic dispersants (e.g. alkylammonium chlorides)
- polyelectronic dispersants (e.g. polybasic acids)
- electroneutral dispersants (e.g. alkylammonium salts of fatty acids)
- bifunctional dispersants (e.g. amino acids)
- non-functional dispersants (e.g. polyethers)

Selection[69,70] of the type used depends on

- final film effects: colour; gloss; resistance to humidity; and toxicological considerations
- paint making considerations: chemical type of powder and medium; efficiency of the mill; and stability to flocculation.

As non-ionic dispersing agents spend a lot of time in the bulk of the paint, they have more of an effect on the coating's resistance to water than the other dispersing agents[71].

4.2.3. Defoamers

Water borne paints are often made using high speed dispersers (Section 2.3.3.). This process allows atmospheric air to become incorporated into the paint, which is trapped to form a foam. While coalescing agents will tend to disrupt this foam, defoamers (which lower the surface tension of the aqueous phase) are an important production aid.

The essential qualities of defoamers (sometimes referred to as antifoams) can be split into three classes[68], although the same compound can act in one or more class. These classes are:

- active compounds - actively destabilising the bubble wall (e.g. long chain alcohols[68] and siloxanes[69])

- spreading agents - allowing the active agents to migrate rapidly (e.g. fatty acid esters)

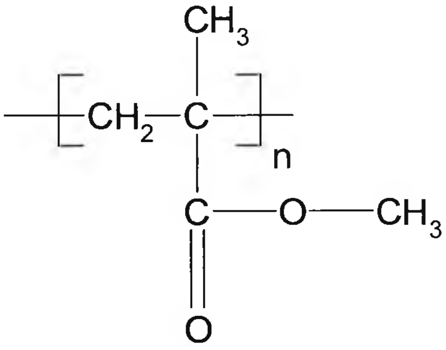
- carriers - allowing the introduction of active and spreading agents to the paint.

Choice of an unsuitable antifoaming agent, or the wrong concentration, can have severe effects on the final film including changing the colour, and cissing (areas of the substrate not covered by paint, also known as fish-eyes and holidays) .

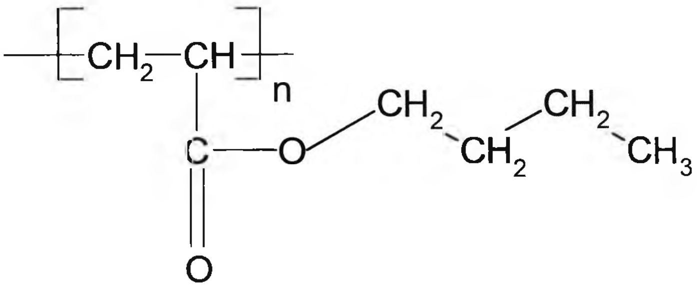
4.2.4. Acrylics

“Acrylic” is the generic name for polymers of acrylic and methacrylic esters, for example poly-butyl acrylate and poly-methyl methacrylate, and their co-polymers. They are common water-borne resins, and are supplied as an emulsion of cross-linked polymer particles in an aqueous medium, often referred to as a latex.

Acrylics are often formulated by reacting together a 'hard' component and a 'soft' component to give a copolymer. A hard component will be more resistant to mechanical damage, but less flexible (and thus less able to follow the expected dimensional changes of wood). Soft components will have complementary properties, and also may be more susceptible to blocking (where dried painted surfaces stick to each other under load). The desired properties of a paint are attained by varying the proportions of hard and soft components. Ulyatt identified the hard component as methyl methacrylate, and the soft as n-butyl acrylate[72]. The hard, brittle qualities are attributed by Morgans[73] to alkyl side chains directly bonded to the polymer backbone, and softness and flexibility to their absence. While n-butyl acrylate has a longer side chain than methyl methacrylate, the butyl group is not bonded directly to the polymer chain, unlike the methyl group in the methacrylate.



Poly-methyl methacrylate



Poly-n-butyl acrylate

A solvent (typically a long chain alcohol, or water soluble long chain ester) is added when the water-borne paint is formulated. This is known as the coalescing solvent, and it is selected to remain in the film until the water has evaporated. In dilute solution it cannot affect the latex, but as the water evaporates, the concentration of the coalescing solvent increases until it can soften the acrylic particles. By this time, the particles are completely packed and the softened particles fuse together forming a coherent film.

4.2.5. Alkyd emulsions

Water-borne alkyds were developed in order to have the properties of an air drying resin, without the environmental and toxicological problems of solvents. Traditional alkyds are only soluble in organic solvents, for example xylene and white spirit. With some formulation adjustments, alkyds can be dispersed in water, as oil in water emulsions.

Alkyds can be emulsified if allowed by the thermodynamics of the system (i.e. if $\Delta G<0$), and if sedimentation can be prevented[74]. In practice, a dispersing agent has to be chosen with great care[74-79]. Anionic dispersing agents (Section 4.2.2.1.) tend to concentrate in the aqueous phase, leading to foaming and flash rusting of steel substrates[74]

Additionally, isophthalic acid is used instead of phthalic anhydride as the dibasic acid (Section 4.1.1.1.1.), because isophthalate polyesters are more resistant to hydrolysis than *o*-phthalate polyesters[77,78]

Low molecular weight components in the alkyd have been found to be water soluble[75,77,78], and this gives alkyd emulsions more Newtonian properties than their solvent borne analogues, in their rheological profile[76,78,79].

Paint is often manufactured under high shear conditions, which results in an increase in temperature. Alkyd emulsions can become unstable when exposed to those conditions and to any pH changes[75,77,78,79]. Drier metal soaps (required to promote autoxidation of the alkyd) can also be prone to hydrolysis (rendering them ineffective), or may initiate flocculation of the alkyd emulsion[79]. If these problems are overcome, the rewards are a "greener" paint than an acrylic[76,78,79], as no coalescing solvents (Section 4.2.4.) are required.

Studies have found that alkyd emulsion paints have similar qualities to solvent borne alkyd paints[76,77,78,79], in terms of penetration of the wood substrate, water permeability and repainting/refurbishment. Alkyd emulsions have oligomer particles (molecular weight 2,000 to 8,000) and this is thought to be why they have better penetration than acrylic emulsions (which are formed of polymer particles with a molecular weight of 100,000 to 1,000,000)[76].

4.2.6. Alkyd-acrylic Hybrids

Acrylics have the quality of being very quick drying (i.e. they only need the solvent to evaporate), but they can have poor chemical and water resistance. Alkyds, through their autoxidation reactions with atmospheric oxygen, have good chemical and water resistance, but remain soft until the additional crosslinking reactions are completed. Hybrids were developed in order to attain the best qualities of each[80]. Acrylic chains can also reduce hydrolysis of waterborne alkyds[81], and improve the dispersion qualities to such an extent that they are sometimes termed[81,82] "self-emulsifying alkyds".

Two types of hybrid are possible: a simple blend of emulsified acrylic with emulsified alkyd; or where the acrylic is polymerised in the presence of an alkyd emulsion. The complex three (or more) component cooking of alkyds (Section 4.1.1.1.) in the presence of an acrylic emulsion, forming a hybrid in this manner is not currently possible.

Blends tended to have more of the qualities of pure acrylics (in terms of hardness and minimum temperature at which a cohesive film will form[80] - the minimum film forming temperature), but may not form good films[80], in that final films can either appear hazy, or crack after a few days.

Hybrids where the acrylic is polymerised in the presence of an alkyd emulsion (although having the same chemical composition as a poor film forming blend) form clear films with a lower film forming temperature than the pure acrylic. Some hybrids may dry to a harder film than either pure alkyd or pure acrylic, although this effect is not universal for all hybrids prepared in this manner[80].

The mechanism for the polymerisation of acrylic in the presence of an alkyd emulsion is recognised[80-82] to be as follows. Acrylic monomer migrates through the aqueous phase, into the hydrophobic alkyd droplets. Once inside the droplets, polymerisation takes place, and the hydrophilic acrylic migrates to the outside of the alkyd droplet. This process forms core-shell emulsions[81,82].

Conjugated double bonds in the drying oil (Section 4.1.1.1.2.) tend to stabilise free radicals formed in the polymerisation of the acrylic due to conjugation[80], and this stabilisation slows the polymerisation down, and can lead to free monomer in the final resin[80]. In cases when two acrylic monomers are used, the most hydrophobic monomer is present at higher concentrations in the final resin[80].

5. Photodegradation of coatings

5.1. General principles

As described earlier, an important function of coatings is to prevent photodegradation of the substrate. Wood is attacked by, among other things, ultraviolet (UV) light, and so one of the requirements for a wood coating is that it absorbs or reflects UV radiation. If light is not blocked by the coating, it can attack a wood substrate, causing loss of strength, defibrillation and colour changes[25,83-86].

5.2. Mechanisms

According to the Grotthuss-Draper law[87,88] only radiation which is absorbed by a system is effective in producing a change to that system. Another important law is the Einstein-Stark law[88], otherwise known[87] as the Law of the Photochemical Equivalent, whereby one quantum of light is absorbed by every molecule undergoing photochemical change. The following equation can be deduced[88]:

$$E = Nh\nu = Nhc/\lambda$$

where

E is the energy absorbed by one mole of reacting molecules

N is the Avogadro number, 6.022×10^{23} mol^{-1}

h is the Planck constant, 6.626×10^{-34} J s

ν is the frequency of the radiation, in hertz

c is the velocity of light in a vacuum, 2.997×10^{8} m s^{-1}

λ is the wavelength of the radiation in metres

thus

$$E = 0.1196 \text{ J } \lambda^{-1} \text{ per mole}$$

The above equation demonstrates why UV light is more damaging than visible and IR, because the energy absorbed increases with decreasing wavelength. The energy absorbed at a specific wavelength is sometimes referred to as one einstein of radiation[87]. Thus for red light with a wavelength of 750 nm, the einstein is about 160 kJ mole^{-1}, and for violet light of wavelength 400 nm it is approximately 297 kJ mole^{-1}. For comparison, the energy of a carbon to carbon single bond is 348 kJ mole^{-1}.

There are two mechanisms by which light can affect coatings. One is termed[89] "photochemical" where the light directly initiates a chemical reaction. The other is termed[89] "photophysical" where the energy of the light is absorbed either as heat or by promoting electrons to higher energy levels. The energy absorbed by photophysical processes can initiate chemical reactions or be released harmlessly as heat or light (for example fluorescence[90]).

Photochemical reactions would be expected to be limited to the organic portion of the coating, namely the resin and any additive such as thickeners. Photophysical reactions could be initiated by one component, for example the pigment, and then the energy transferred to, for example, the resin.

Coatings absorb electromagnetic radiation[91-93] of specific wavelength. Some wavelengths (for example red in the visible spectrum) are less likely to degrade a polymer (P), but others, for example ultraviolet, have sufficient energy to cleave covalent bonds, forming free radicals[89] ($P\bullet$ and $X\bullet$, where $X\bullet$ is the leaving group), via a higher energy state (P^*).

$$P \xrightarrow{h\nu} P^* \longrightarrow P\bullet + X\bullet$$

Resins which are transparent to damaging ultraviolet light may still be degraded since the radiation may be absorbed by additives[89,90,94] or impurities which may form free radicals directly or transfer their energy to the polymer either partially, or completely in the form of heat. An excited charge transfer complex, which is called an "exciplex", may be formed. As with excited molecules, the exciplex can either break down into the original components and fluorescence, or produce vibrational energy (heat), or initiate a chemical reaction, usually by a radical process[89]. The donor can also, of course, be present in the same molecule as the acceptor, either as a repeating unit, or as an impurity. Thus the following general reactions can be drawn[90] with the accepted symbols[89] of D representing a donor (the additive or impurity), A the acceptor (resin), v vibration energy, and $(DA)^*$ an exciplex:

$$D^* + A \longrightarrow D + A^*$$

$$D^* + A \longrightarrow Dv + Av$$

$$D^* + A \longrightarrow (DA)^*$$

$$(DA)^* \longrightarrow D + A + h\nu$$

$$(DA)^* \longrightarrow D\bullet + A\bullet$$

Transference of energy from a donor to an acceptor can proceed either intermolecularly or intramolecularly. Intramolecular transference can occur by three distinct pathways[90]:

- hopping across chromophores
- moving to, and then along, the polymer backbone
- moving across loops in the polymer backbone.

Transference of energy across loops in the polymer backbone (where the polymer coils until two points are near enough for transference to take place) has been suggested in order to explain solvent effects, where reactions of a polymer in solution can be influenced by its concentration, and also the polarity of the solvent. This mechanism could also be present in solvent free paint films.

On formation of radicals (initiation[89] or photolysis[91]), further reactions occur (propagation[89] or autoxidation[91]) some requiring energy in the form of light, and others able to proceed without further energy. The polymer radicals first react with atmospheric oxygen forming peroxy radicals. These eventually lead to ethers, peroxides or new polymers with a different molecular weight[89,91].

5.3. Norrish reactions

Between 1932 and 1938, Norrish studied, with various co-workers, photochemistry of various molecules[95-108]. While this early work was carried out with short wavelength UV light, Guillet[109] notes that Norrish reactions are important in the degradation of polyesters and other polymers.

Most of Norrish's studies were with ketones and aldehydes[99,101-108]. Two photochemical reaction mechanisms were named after him, and these are referred to as Norrish Type I and Type II reactions[89,93,94,98,104-108]. Bamford and Norrish[107,108] identified a third mechanism, Type III, but this is considered rare[108].

It is widely considered[89,109-112] that Norrish Type II reactions proceed via a six membered cyclic intermediate involving radicals. This conflicts with Norrish's findings that a Type II mechanism accounts for at least some of the photodegradation products of cyclic ketones[104] and methanoic acid[108].

Bamford and Norrish[107] also found that aldehydes and ketones following a Type II mechanism were readily decomposed by UV radiation both in solution and at room temperature. If free radicals were involved, they would be expected to be quenched by the solvent[107].

5.4. Alkyds

The structure of a dried alkyd film is very complex (Section 4.1.1.4.). We can, however, look at an idealised photochemistry by considering it as two separate polymers, a polyester and a crosslinked hydrocarbon derived from the drying triglyceride oil.

The mechanisms described in sections 5.2 and 5.3 above can apply to alkyds. Tsubouchi and Doi[113] reported that alkyl, ether and ester linkages in alkyds are destroyed by chain scission or hydrolysis during natural weathering, and the degradation products leached from the coating.

The polyester component of the alkyd can degrade by Norrish Type I and Type II mechanisms, although Guillet[109] and Ahola[110] both note that the Type I reaction is more important in the solid phase.

The chemistry for the photodegradation of the crosslinked hydrocarbon component is less easy to understand. Hodson and Lander[115] observed a decrease in the absorptions from -CH_3 and -CH_2- groups in IR spectra of alkyd paints on ageing. This was attributed to chain scission reactions. This conclusion is supported by unpublished work by the present author, who found that soya oil (a semi-drying vegetable oil[115] used as a component of many alkyds[116]) dried with cobalt soap alone (Section 4.1.1.3.) degraded from a coherent film to a liquid after a few weeks. This liquefaction proceeded, at ambient temperature, with a variety of cobalt soaps, and both in the light and in the dark. The films were examined, at PRA, by W. R. Springle and A. L. Smith, who found no evidence of microbiological activity, indicating that the liquefaction was solely due to a chemical reaction.

Hodson and Lander[114] also reported an increase in -COOH and -OH. The increase in alcohol groups conflicts with Crecelius et al[117], who reported that they were lost. Crecelius also found that carbonyl groups were lost.

The discrepancy in the formation or loss of -OH groups can be explained by competition between Norrish Type I reactions (which lose oxygen as carbon monoxide), and a radical reaction with absorbed atmospheric oxygen. Both experiments used accelerated weathering, but Hodson and Lander[114] used a QUV Weatherometer, fitted with type A lamps (Section 2.4.3.2.) whereas Crecelius et al[117] used a much more intense Mineralight ultraviolet lamp Model No. 343. The QUV exposure was over twenty-four days (288 hours) whereas the Mineralight lamp experiments only lasted a maximum of 38 hours. It is reasonable to assume that the short, intense, UV exposure caused a localised depletion of oxygen over the coating, favouring the Norrish Type I reaction, whereas the longer QUV experiment allowed air changes over the panel, permitting a radical reaction with oxygen.

5.5. Acrylics

Acrylates and methacrylates undergo similar photochemical reactions[118]. While aliphatic acrylics do not absorb over much of the UV range, they can undergo hydrogen abstraction and Norrish reactions. Rånby[119] notes that absorption in the near UV increases during photolysis.

Tsubuchi and Doi[113] observed acrylic resins degrading by chain scission and Norrish reactions on natural exposure. MacCallum[120], however, notes that Norrish Type I reactions are initiated at 254 nm (the wavelength emitted by a low pressure mercury lamp[121]). This wavelength would be absorbed by the Earth's atmosphere and is not normally present at the earth's surface.

MacCallum[120] also made the interesting observation that, at ambient temperature, acrylates cross-link, while the methacrylates undergo the more expected chain scission. This observation is confirmed by Ahola[110]. They do not identify exactly where the acrylates cross-link, but Rabek[118] notes that it occurs across two polymer chains, after formation of a radical, from the loss of carbon monoxide.

Torikai et al[121] reported evidence of aldehydes and ketones after polymethyl methacrylate was exposed to UV light, indicating that Norrish Type II or Type III reactions also take place. Mitsuoka et al[122] confirmed the Type III mechanism whilst investigating the effect of air on the degradation of polymethyl methacrylate by UV light.

Lemaire et al[123] found that the degradation of polymethyl methacrylate was exclusively due to donor chromophores, i.e. from impurities, (Section 5.1.). He also found that these impurities were leached toward the surface, and that if the degraded surface was removed to expose a fresh, undegraded surface, the rate of photodegradation was reduced. This work emphasises that essential additives to water-borne coatings, thickeners (Section 4.2.1), dispersing agents (Section 4.2.2) and defoamers (Section 4.2.3) have great potential for increasing photochemical degradation.

5.5. Pigments

If light is absorbed by pigment or extender, it will usually be harmlessly converted to heat. Not all extenders will absorb the most damaging wavelengths of light, and some inorganic compounds actively promote photodegradation of binders. The photochemistry of two common paint pigments, iron oxide and titanium dioxide, will be considered.

5.5.1. Iron oxide

Iron oxide is widely used as both an opaque and a semi-transparent pigment (Section 2.2.2.) owing to its wide UV absorbance[91,93]. Rasti and Scott[124] found that iron oxide in the form Fe_2O_3 retarded the photo-oxidation of linseed oil based artists' paint, but Rabek[125] notes that the iron (III) ion can be photoreduced at 230 nm to the less stable Fe(II) ion, initiating radical degradation of a polymer matrix. Three of these reactions require water as a ligand, and two produce hydroxy radicals. These reactions could be important for paints with, for example, early morning sun through dew, sunshine after rain, or even if water is absorbed in the paint, though it must be stressed that light wavelengths as short as 230 nm will not be present in terrestrial solar radiation. Information on the effectiveness of these processes at longer wavelengths is not available.

Iron ions can also react directly with hydroperoxides to form peroxy and oxy radicals[126] and can also with hydrogen peroxide[109] (possibly formed from other reactions), by photo-Fenton reactions. Reactions with polymeric peroxides may be similar. Additionally, reactions with oxygen are possible[109].

5.5.2. Titanium dioxide

Titanium dioxide exists in three crystal structures[126]: anatase, brookite and rutile. Brookite is not used as a pigment[127]. The rutile form is most favoured as a pigment, owing to its relative photo-inactivity[93,128], and its ability to absorb UV light strongly[91,93,129]. Anatase titanium dioxide is known to actively promote photocatalytic degradation[91,93,128] due to a deformed surface of the crystal lattice[91], but the photoactivity of rutile titanium dioxide is also well known[128-131]. Paradoxically, Simpson[130,131] observes that for very durable resins, the primary degradation process is due to titanium dioxide. This is because titanium dioxide can degrade any resin, even those formulated to resist chain scission, hydrolysis, etc.

This photoactivity explains[91,93,128] the tendency of titanium dioxide pigmented paints to “chalk”, a process whereby the binder erodes, leaving the pigment exposed; the fine pigment is easily brushed off, and resembles (at least superficially) blackboard chalk (Section 2.4.1., Figure 2.1). The difference in photoactivity means that for paints formulated with rutile titanium dioxide, the resin tends to erode with the pigment on "pedestals" due to UV shading, whereas anatase titanium dioxide sits in pits due to photocatalytic oxidation[128].

In addition to its photocatylitic capabilities, titanium dioxide can also react with oxygen, to form singlet oxygen, (which can subsequently form atomic oxygen radicals)[128]. These species can also degrade a polymer[132].

When water and oxygen are both present, a species described by Rabek[128] and Tang et al[129] as (Ti^{4+},OH^{-}) has been reported on the surface of the crystal. The structure of this species is not reported. It is, however, known to react to light, which excites an electron from the valence bond, to the conduction band[128-131], forming[93,128,129] an electron and hole, collectively termed an exciton[128] (e/p or TiO_2(e/p)). For an exciton to be formed, the energy of the light must be greater or equal to 3.05 electron volts (eV) for rutile, and 3.30 eV for anatase titanium dioxide[128].

There appears to be some confusion as to the mechanism of subsequent reactions. Certainly, hydroxy radicals, hydrogen peroxide, dioxygen radicals, and hydroperoxy radicals are formed, but authors differ on the mechanisms. Wicks et al[93] and Tang et al[129] both state that first the electron of the exciton reacts with adsorbed oxygen. Tang et al[129] suggests that the $O_2\bullet^{-}$ radical would be annihilated by the positive hole, forming singlet oxygen or atomic oxygen radicals, whereas Wicks et al[93] postulates that the hole will react with water, forming hydroxy radicals and hydrogen peroxide. Rabek[128], however, suggests that the hole will instead react with the surface hydroxide ion, with the titanium changing from oxidation state 4, to 3, and then back again. The radicals produced in all three pathways can initiate degradation.

In order to limit photodegradation, commercial titanium dioxide is coated[91,93,114] with alumina, silica or zirconia. Simpson[130,131] states that these coatings serve by recombining the electron with the hole.

5.7. Summary

One important role of coatings is to prevent photodegradation of the substrate. In order to do this they either absorb or reflect damaging light. If the resin absorbs light of sufficiently short wavelength, in the UV, bonds can cleave allowing radical degradation reactions. Even if the resin does not absorb damaging radiation directly, impurities and additives can absorb, then pass the energy to the resin, also allowing radical degradation to occur.

Pigments have a net beneficial effect, protecting both coating and substrate from photodegradation. They do, however, have a well documented photoactivity, and so can contribute to the photodegradation of coatings.

6. Systems Studied

6.1. Introduction

For this study, seven coating systems were studied. These were chosen to reflect the common forms of coatings for the exterior protection of wood available to the 1990s domestic market. Due to the short span of the project, the systems were formulated (Section 2.1.) to fail within a few years, while still being representative of the coating type. None of the coatings had UV stabilisers. The pigment concentration in opaque coatings were not optimised (the pigment volume concentration has dramatic effects on the properties of the coating[3]). Biocides were not added to any paint. The model formulations had the added advantage that the compositions were less confidential.

Four solvent borne paints were studied, three with a modern "semi-flexible" alkyd resin (with differing pigmentation), and one based on a traditional alkyd resin as a control. Three water borne coatings were also studied, two with the same acrylic resin, but different pigments, and the third being an alkyd-acrylic hybrid.

The seven systems studied were:

Long oil semi-flexible alkyd in solution in organic solvent

- i. unpigmented to give a clear coating, identified as System 1
- ii. pigmented with iron oxide to give a semi-transparent stain, identified as System 2
- iii. pigmented with dolomite and titanium dioxide, to give an opaque coating, identified as System 3

Traditional alkyd in solution in organic solvent formulated as a primer:undercoat:topcoat opaque system. This "traditional" system served as a control and was identified as System 7.

Acrylic suspended in water

- i. pigmented with iron oxide to give a semi-transparent stain, identified as System 4
- ii. pigmented with mica and iron oxide to give an opaque coating, identified as System 5

Alkyd/acrylic hybrid suspended in water pigmented with titanium dioxide, to yield an opaque coating, identified as System 6

6.2. Alkyds

6.2.1. Modern formulation

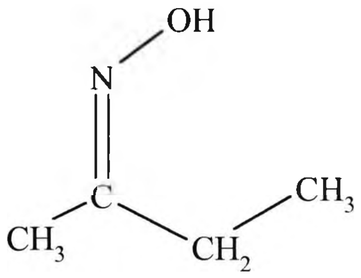
Systems 1, 2 and 3 were formulated to reflect the current trend whereby the same coating is used as primer, undercoat and topcoat. For these systems, a modern alkyd resin, Synolac 6005W, was used with three levels of pigmentation: clear; semi-transparent; and opaque.

Synolac 6005W, manufactured by Cray Valley Products Ltd, is described[116,133] as a flexible alkyd for long life exterior wood coatings, having an oil length of 65%. The oil type is linoleic and a mixed polyol has been used. A flexible thixotropic alkyd, Synolac 6006W was added to improve the rheological profile. This thixotropic alkyd is specifically designed for use with Synolac 6005W, and has a similar oil type linoleic[116,134], with a length of 65%. The thixotropy is developed by the addition of a polar solvent, for example methoxypropanol. Other details of the two resins, 6005W and 6006W, are not revealed for commercial reasons.

The three pigmentation conditions studied were

1. unpigmented (System 1)
2. pigmented with iron oxide (at 4% of the liquid coating) as a semi-transparent stain (System 2)
3. pigmented with titanium dioxide and dolomite (at a total of 39% of the liquid coating) as an opaque white (System 3).

An anti-skinning agent was added to the paints. Anti-skinning agents inhibit autoxidation reactions in the can, but are volatile, and so escape from a film on application, allowing the film to cross-link. Consequently, methyl ethyl ketoxime (which is usually abbreviated to MEK or, in cases when it may be confused with methyl ethyl ketone, ME ketoxime) was added to the formulations as the anti-skinning agent. Even so, the cans were flushed with nitrogen to reduce further the risk of skinning.



Methyl ethyl ketoxime

The thickening agent, methoxypropanol ($CH_3OCH_2CH(OH)CH_3$) was supplied, as Dowanol PM, by the Dow Chemical Company Ltd.

Iron oxide paste, Sicoflush yellow 1916 C4, was supplied by BASF PLC.

Titanium dioxide RCR2 was supplied by Tioxide Specialities Ltd.

Calcium magnesium carbonate (dolomite) was supplied as Microdol Extra, by Norwegian Talc Ltd.

The following table details the formulations of each of the three coatings, in the order of addition. These were prepared at PRA by A. F. Sherwood, who used a high speed disperser (Section 2.3.3.).

Table 6.2.1. : Figures shown are percentage by weight

Component	System 1 Clear alkyd	System 2 Alkyd stain	System 3 Alkyd opaque
Alkyd resin, Synolac 6005W	57.70	40.33	32.79
Alkyd thixotropic resin, Super Gelkyd 6006W	21.08	14.74	11.98
Manosec cobalt octoate 12%w/w in white spirit	0.44	0.30	0.25
Manosec zirconium carboxylate 24%w/w in white spirit	0.33	0.23	0.19
Manosec calcium carboxylate 10%w/w in white spirit	1.04	0.73	0.59
Methyl ethyl ketoxime	0.22	0.16	0.13
Methoxypropanol	2.32	1.62	1.32
White spirit	16.87	31.16	14.17
Iron oxide pigment, Sicoflush yellow 1916 C4 (40% iron oxide, 60% linseed oil alkyd in an organic solvent)	0	10.73	0
Titanium dioxide, RCR2	0	0	22.16
Calcium magnesium carbonate, Microdol Extra	0	0	16.42

6.2.2. Traditional formulation

A traditional alkyd based on Synolac 66W (manufactured by Cray Valley Products Ltd) was used as a comparison, but only in the form of an opaque white three coat system. Collectively, these three coats were named System 7, since this paint was intended to serve as a control for the water borne systems as well as the solvent borne. Synolac 66W has[116] an oil type linoleic, with a length of 65%, and pentaerthritol as the polyol.

The primer was pigmented with titanium dioxide RCR2 supplied by Tioxide Specialities Ltd, talc AT1 by Norwegian Talc Ltd and barium sulphate Barytes EW30 by Sachtleben Chemie GmbH.

The undercoat was pigmented with the same grade of titanium dioxide, calcium carbonate Millicarb by Croxton and Gary Ltd and china clay Devolite by ECCI Ltd.

The topcoat was pigmented with just titanium dioxide RCR2.

This three coat system was made by A. F. Sherwood at PRA, using a high speed disperser (Section 2.3.3.). The exact formulations are detailed in the table below. The components are listed in the order of addition.

Table 6.2.2. : Figures shown are percentage by weight

Component	Traditional alkyd primer	Traditional alkyd undercoat	Traditional alkyd topcoat
Alkyd resin, Synolac 66W	39.80	42.17	55.06
Titanium dioxide, RCR2	12.97	15.91	26.47
Talc, AT1	4.05	0	0
Barium sulphate, Barytes EW30	23.74	0	0
Calcium carbonate, Millicarb	0	19.24	0
China clay, Devolite	0	4.15	0
Manosec cobalt octoate 12%w/w in white spirit	0.10	0.11	0.14
Manosec zirconium carboxylate 24%w/w in white spirit	0.15	0.16	0.20
Manosec calcium carboxylate 10%w/w in white spirit	0.48	0.51	0.65
Methyl ethyl ketoxime	0.04	0.05	0.06
White spirit	18.67	17.70	17.42

6.3. Acrylics

The acrylic paints used in this study were made and supplied by Rohm and Haas Ltd, who formulated two coatings based on the same resin, but with different pigments. The formulations were such that the same coating could be used as primer, undercoat and topcoat. The formulations are detailed in Tables 6.3.1 and 6.3.2. The function of the additives is given in Sections 4.2.1. to 4.2.3., and the reason for using two grades of iron oxide in Section 2.2.2..

Table 6.3.1 : Acrylic stain

Component	Percentage by weight
Acrylic emulsion, E 1381	37.10
Iron oxide, Jaune Luconyl 1916	1.54
Defoamer, Nopco NDW	0.18
Wetting agent, Triton X-114	0.82
Urethane thickener, QR-1020	2.73
Acrylic thickener, TT-935	27.95
Propylene glycol	12.41
Water	17.27

Table 6.3.2 : Acrylic opaque

Component	Percentage by weight
Acrylic emulsion, E 1381	40.54
Iron oxide, 3920	8.19
Mica, Micro Mica W1	20.84
Defoamer, Nopco NXZ	0.39
Wetting agent, Triton CF-10	0.16
Urethane thickener, QR-1020	1.79
Cellulose thickener, Natrosol 250 MR	3.10
Dispersing agent, Orotan 731	0.40
Ethylene glycol	3.10
Texanol[‡]	1.09
Water	20.40

[‡] Texanol is reported to have the structure[135]:

$(CH_3)_2CHCH(OH)C(CH_3)_2CH_2OCOCH(CH_3)_2$, but unpublished analysis by the author suggests that this component has at least two isomers.

The materials were supplied as follows:

iron oxide Jaune Luconyl 1916	BASF Plc
iron oxide 3920	Bayer UK Ltd
Nopco NDW and Nopco NDZ	Henkel Performance Chemicals
Triton X-114, Triton CF-10, QR-1020, TT-935, and Orotan 731	Rohm and Haas Ltd
Natrosol 250 MR	Aqualon UK

6.4. Hybrid

The hybrid system used in this project was made by Jotun BV, and was made using Dynotal T-75-W and Dynolex A-081-W. Dynotal T-75-W is an alkyd designed by Dyno Industrier for use in exterior paints either alone or with acrylic emulsions, in this case Dynolex A-081-W[116].

The thickener used was a cellulose type (Section 4.2.1.1.), Natrolsol H4BR. Two dispersing agents (Section 4.2.2.) were used, one being sodium tripolyphosphate and the other Orotan 731 SD.

Foammaster SB was used as the defoamer (Section 4.2.3.).

This coating was formulated as an opaque system with titanium dioxide as the pigment so that the same paint could be used for primer, undercoat and topcoat.

The materials were supplied as follows:

Dynotal T-75-W, Dynolex A-081-W, and Dynoadd D15	Dyno Industrier
Titanium dioxide RNCX	Kronos Titan
Natrosol H4BR	Aqualon UK
Orotan 731 SD	Rohm and Haas Ltd
Foammaster SB	Henkel Performance Chemicals

Table 6.4. : Hybrid

Component	Percentage by weight
Alkyd emulsion, Dynotal T-75-W	28.82
Acrylic emulsion, Dynolex A-081-W	22.36
Titanium dioxide, RNCX	16.65
Cellulose thickener, Natrosol H4BR	0.57
Dispersing agent, sodium tripolyphosphate	1.90
Dispersing agent, Orotan 731SD	0.29
Defoamer, Foammaster SB	0.38
Drier metal blend, Dynoadd D-15	1.33
Methyl ethyl ketoxime	0.19
Ammonium hydroxide (for adjustment to pH 9.2)	a few drops
White spirit	0.95
Water	26.56

7. Substrates and their exposure

7.1. Introduction

Three different substrates were used:

Scots Pine wooden panels
aluminium panels
high density polythene panels.

The coatings were formulated for application to wood, so wood panels were preferred. These were used for surface determinations, for example Fourier Transform Infra-red Spectroscopy.

For some tests, wood would interfere, for example, determination of the organic content of the films on ageing. For these tests, an aluminium substrate was used. As many wood coatings are also suitable for application to metal, aluminium was the preferred alternative substrate.

However, entirely detached free films were required for dynamic mechanical thermal analysis. In order to prepare these, it was necessary to use high density polythene panels, to which the adhesion of the films was low enough to allow easy separation, but high enough to withstand natural exposure.

7.2. Scots Pine wooden panels

Scots pine (Section 3.2.1.) wooden panels were supplied by the Building Research Establishment (BRE) at Garston in the form of 600x100x20 mm panels selected to be knot free, tangentially sawn, sapwood. The grain of the wood ran along the longest dimension. No preservative was used in the wood in order to simulate the conditions found in most domestic circumstances. The panels were painted, with the seven systems detailed above (Chapter 6), on the bark side and both longitudinal edges by N. L. Zealey.

Three coats of each system were applied; with the exception of System 1, the clear alkyd based on Synolac 6005W which was applied as four coats and System 7, the traditional alkyd, which was applied as primer, undercoat and topcoat as the three coats.

Each coat was allowed to dry for at least twenty-four hours before recoating.

The back of the panel, the pith side, was treated with a single coat of a dilute solution of alkyd Synolac 66W in white spirit, (described above). This was thinned with white spirit until it had a solids content of 10% w/w, and was dried using cobalt, zirconium and calcium. This was intended to duplicate the building practice of only painting the exposed faces, while acknowledging that the unexposed faces have some small degree of protection. The end grain was sealed using two coats of the dilute alkyd solution (this would be adsorbed into the grain better than a higher solids coating[136]), followed by a single coat of good quality wood primer, and finally by a flexible two-pack polyurethane potting compound supplied by RS Components Ltd.. The potting compound was inspected throughout the exposure period and additional coats applied, as necessary, to ensure a continuous protection. After being stored indoors for one month, a total of 642 wooden panels were exposed at both a rural and an urban location (147 panels were required for the results reported in Chapter 9, with the remainder being used for the main PRA project described in Chapter 1).

The rural location was in the grounds of the University College London Mullard Space Science Laboratory near Holmbury St Mary, Surrey, and the racks were sited at ground level. The location of the site was chosen to minimise shading by trees.

The urban location was on the roof of the Paint Research Association, Teddington, Middlesex. These panels experienced very little, if any, shading.

At both sites, the panels were exposed in a southerly orientation (with the grain of the wood running along the north-south axis) at a gradient of about 1 in 24, i.e. about 2.5° to the horizontal, using a cable tie with sufficient tautness to secure the panel to the rack without damaging the soft wood. This angle was chosen to increase the severity of the exposure. Surplus rainwater could run off the panel, but the panel remained far wetter than a more conventional 45° angle to the horizontal.

Every three months a set of three panels of each of the seven systems were returned to PRA, and visually assessed for cracking, flaking, blistering, soiling, cupping and moisture content by a team led by N. A. R. Falla. A 200 mm length ($\frac{1}{3}$ of the total) was then cut off, and the remaining section returned for exposure after re-sealing the end grain as described above. The 200 mm sections were cut into two 100x100x20 mm panels.

For each system, three of these six square panels from both sites were subjected to microbiological investigations by W. R. Springle and A. L. Smith. The rest were cleaned by N. L. Zealey by lightly rubbing with tissue paper soaked with distilled water.

The panels exposed at Holmbury were subjected to the following tests:

colour difference by H. D. Mehta and K. E. Walker (reported elsewhere[49]);
gloss level by H. D. Mehta and K. E. Walker (reported elsewhere[49]);
cross hatch adhesion by N. L. Zealey (reported elsewhere[49]);
microscopic examination by D. Honan (not reported);
and Fourier transform infra-red spectrometry - photoacoustic spectroscopy (FTIR-PAS) - reported below (Section 9.3.).

Those panels exposed at Teddington remaining after microbial examination were used for water permeability studies by H. D. Mehta and N. L. Zealey (reported elsewhere[49]). The water permeability studies required a surface area of 1,000 cm^2, and so the panels exposed at Holmbury were unsuitable (having had sections removed for microscopic examination and FTIR-PAS, and other areas of the surface damaged by cross hatch adhesion studies). Prolonged contact with water (as a result of the water permeability studies) was thought to render the Teddington panels unsuitable for other tests.

7.3. Aluminium panels

Aluminium panels were 76x15x0.6 mm chromium treated panels as supplied by the Q-panel company[137]. It is recognised that aluminium has a reactive surface, but the chromium treatment is known to passivate the surface[138,139].

The number of coats applied, and the average film thicknesses[140] (as determined by N. L. Zealey) are detailed in Table 7.3.

Table 7.3. - Aluminium panel coating thicknesses

Description	System number	Number of coats	Typical dry film thickness (in μm)
Clear alkyd	1	3	53
Alkyd stain	2	4	38
Alkyd opaque	3	3	57
Traditional alkyd	7	3*	89
Acrylic stain	4	4	117
Acrylic opaque	5	3	70
Hybrid opaque	6	3	71

*As one coat each of primer, undercoat and topcoat

These panels were exposed under the same conditions as described above, except that the exposure gradient was about 1 in 3.5 (about 16° to the horizontal).

Every three months, at the same exposure intervals as the wooden panels (Section 7.2.), one panel of each of the seven systems was returned to PRA. Panels exposed at Teddington were subjected to microbial studies by W. R. Springle and A. L. Smith at the Paint Research Association, Teddington and were deemed to be unsuitable for further testing. Only those panels exposed at Holmbury St Mary were subjected to the following tests:

colour by H. D. Mehta and K. E. Walker (reported elsewhere[141-144]);

Buchholtz hardness[145] by N. L. Zealey (reported elsewhere[141-143,144]);

resistance to cracking[147] by T. Glazier and T. J. Winter (not reported).

Colour testing is a non-destructive method, Buchholtz hardness determinations leave small cuts in the surface (and were so positioned so that they could not promote cracking). The resistance to cracking test involved bending, and permanently deforming, the panel round a conical mandrel.

After these tests, the coating was scraped off using a scalpel. This yielded between 0.25 g and 1.70 g of coating, dependent on the film thickness, and the density (the opaque systems weighing more than the clear and semi-transparent coatings). These scrapings were divided, by eye, into four portions. Between 0.04g and 0.10g was reserved for non-volatile and ashing determinations, and between 0.0018 g and 0.0050 g for differential scanning calorimetry (DSC) analysis. The remaining two portions were approximately equal (between 0.1 g and 0.8 g), one portion being subjected to water extraction, and the other to dichloromethane solvent extraction.

7.4. High density polythene panels

High density polythene panels were used solely to prepare specimens for dynamic mechanical thermal analysis (DMTA), and were cut from a large sheet of high density polythene into panels approximately 150x100x1 mm.

It was found that DMTA required detached films with a film thickness of at least 100 μm. As the other panels were being painted while this development work was in progress, these panels were exposed to a different time sequence to the other substrates, lagging behind by approximately six months.

The number of coats of paint was calculated using simple proportion based on the number of coats of paint applied to the aluminium panels, and the average total film thickness (Section 7.3., Table 7.3.). The number of coats applied to these panels is summarised in Table 7.4. The actual film thicknesses are expected to differ from the calculated value of 100 μm as different substrates have a different "feel" when being painted, and so the “loading” on the panel will differ.

Table 7.4. - High density polythene panel film thicknesses

System number	Description	Number of coats	Typical dry film thickness (μm)
1	Clear alkyd	6	305 ± 42
2	Alkyd stain	10	289 ± 12
3	Alkyd opaque	6	163 ± 14
4	Latex stain	4	97 ± 6
5	Latex opaque	4	127 ± 17
6	Hybrid opaque	4	90 ± 9
7	Traditional alkyd*	4	134 ± 18

*applied as primer, undercoat and two topcoats.

All the paints were applied by N. L. Zealey. As with the other panels, at least twenty-four hours elapsed between recoating and the coated panels were kept indoors for one month before placing them outside. Exposure time was calculated from the first day of external exposure.

7.5. Exposure

The main sets of panels (wood and aluminium - Sections 7.2. and 7.3.) were exposed in August, and the high density polythene panels were exposed the following December. Exposure of young paints to summer sun is thought to be more severe than commencing exposure in the winter, but this effect was ignored for the purpose of these experiments. Additionally, the thickness of the films on polythene does not reflect a normal film thickness, and so could induce anomalies into the experimental results (due to, for example, retained autoxidation compounds, reduced water permeability, increased heterogeneity due to paint layers nearest the substrate not being weathered to the same extent as those layers near the surface).

These panels were exposed in the same orientation as the aluminium panels (slightly steeper than the wood panels), but only at Teddington. Each polythene panel was supported by a steel panel (painted with a good quality anti-corrosive paint by T. Glazier) in order to prevent deformation of the plastic.

8. Techniques used in this study

8.1. Introduction

Seven investigations were performed in the part of the work reported here. Each was used for each set of panels withdrawn every four months (Chapter 7). These seven investigations, and the information about the coating that they provide, were:

- differential scanning calorimetry (DSC)
  Determination of the variation on ageing of the T_g of each coating

- dynamic mechanical thermal analysis (DMTA)
  Measurement of the cross link density, flexibility and plasticisation of each coating at various temperatures, and how they change with time

- Fourier transform infra-red photoacoustic spectroscopy (FTIR-PAS)
  Examination of any changes in the chemical structure of the resin at the surface as a result of ageing

- Determination for any volatile material entrapped in the coating, whether degradation compounds, or adsorbed molecules
  Determination of low molecular weight plasticisers by weight loss on heating

- Determination of polar non-volatile components in the coating
  Determination of higher molecular weight plasticisers - gravimetric water extractable material content

- Determination of non-polar non-volatile material in the coating
  Determination of higher molecular weight plasticisers - gravimetric dichloromethane extractable material content

- Changes in the pigment volume concentration (due to erosion) on ageing
  Determination of the organic content by ashing

8.2. Differential Scanning Calorimetry

8.2.1. Introduction

In a differential scanning calorimetry (DSC) plot of heat capacity (or enthalpy) against temperature where there is a point of inflexion, the temperature at which it occurs is termed the T_g (glass transition temperature). This is the point at which there is a disproportionate change in the physical properties of a polymer (e.g. hardness and volume).

The term T_g was initially limited to amorphous liquids by Fox and Flory[148], who preferred the term "brittle temperature" or "second-order transition temperature" for long chain polymers. Flory later defined the T_g as a state of iso-free volume[149], meaning that the intramolecular distance between polymer chains changes suddenly at the T_g.

These early studies concentrated on low molecular weight polymers, which are often liquids above their T_g. Certainly this early work recognised that polymers in the glassy state are not thermodynamically stable, and that there are kinetic limitations, in that the polymer does not have enough energy to move to the most stable position, or orientation. This means that the T_g is dependent on cooling rate, but less dependent on heating rate.

With low molecular weight polymers, the T_g is easy to determine - the polymer changes from a liquid into a solid (the "glass"). When longer chain polymers are studied, the T_g is less easily observed, and it is necessary to study the physical changes that occur over the T_g.

Many physical characteristics change abruptly over the T_g, such as density, durability, enthalpy, hardness, heat capacity, length, porosity, specific heat and stiffness. As these characteristics are different, it is not surprising that there are discrepancies in the value of T_g determined by different methods; Rodriguez and Long[150] compared hardness and heat capacity, by a microindenter and a DSC respectively, and found up to 7 °C difference in the systems studied, which was considered reasonable.

Differential scanning calorimetry (DSC) originally measured the temperature difference between a sample and a reference. More recently, as an alternative, the sample and reference are maintained at the same temperature, and the power variation required to maintain this is recorded. The second technique tends to be less sensitive, although more convenient.

In general terms the less sensitive the DSC, the more sample is required to give a measurable difference, and the broader the thermal event appears to be (due to the time lag in conduction from the site of heating to the point furthest away). This broadening tends to flatten small signals which decreases the detection limit further.

8.2.2 Calculation of T_g

Conventionally, the T_g is reported in one of three ways, either: the start of the sharp increase (favoured[151] by the coating industry); halfway up the increase (preferred[151] by the plastics industry); or as the sharp increase starts to level off. The temperature difference between the start and end of the transition can be 70°C apart. For this present work, use was made of the Richardson equations[152], which more closely corresponds with the values obtained by dilatometry, and approximate to the "mid-point" T_g (Figure 8.2). These rely on the slopes of the heat capacity versus temperature graph being constant before and after the T_g. Although the start temperature is favoured by the coatings industry, this study monitored the change of T_g with exposure, and thus the actual value is less important than the trend. The trend for the start temperature could, conceivably, be different to that determined here, if the T_g becomes broadened or sharpened with exposure.

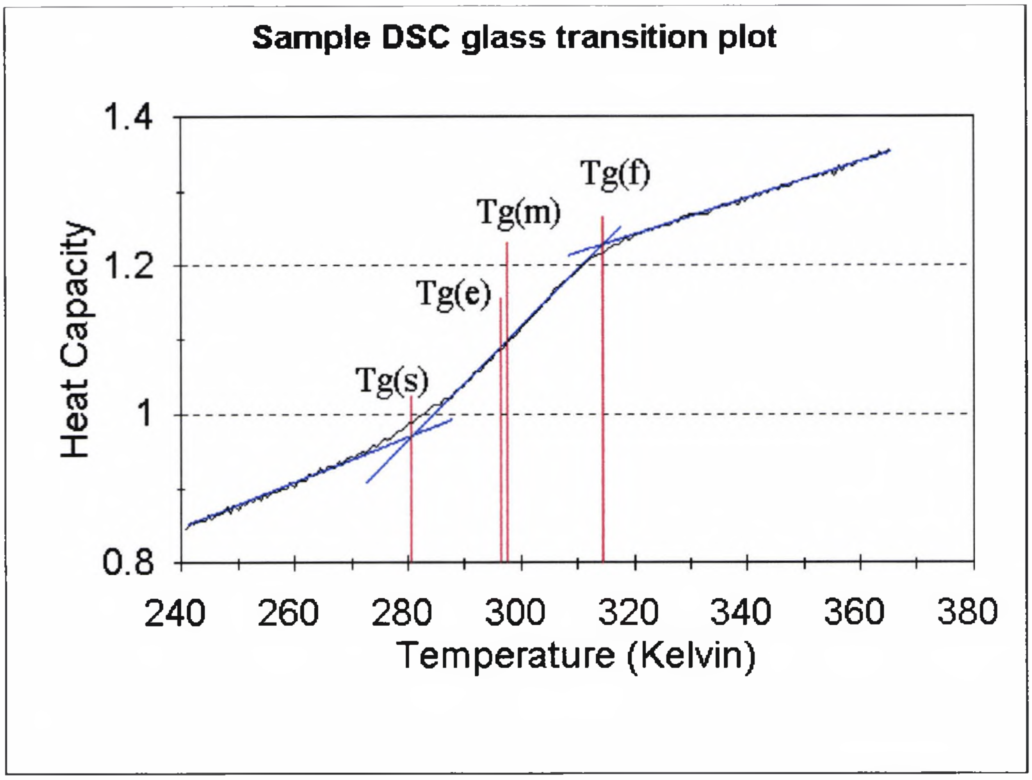


Figure 8.2. Glass transition plot of an unexposed traditional pigmented alkyd. The black trace is from the original data, blue lines are the intersection lines, and the red lines show the T_g s.

Tg(s) is the start T_g;
Tg(e), the calculated T_g using the Richardson Equation, and used here;
Tg(m), the mid-point T_g;
and Tg(f), the final T_g.

Linear equations of the Y = mX + c type were deduced (by the computer controlling the DSC) for the parts of the DSC graph corresponding to the amorphous and glassy states.

Thus:

$$C_{pa} = m_aT + c_a \qquad 8.1.$$

$$C_{pg} = m_gT + c_g \qquad 8.2.$$

where

C_{pa}, C_{pg} are the heat capacities in the amorphous state and the glassy state respectively
m_a, m_g are the gradients of the straight lines for the amorphous and glassy states respectively
T is the temperature in kelvin
c_a and c_g are the intercepts for the Y = mX + c type lines for the amorphous and the glassy states respectively

Since enthalpy (H) = $\int C_p dT$, if equations 8.1. and 8.2. are integrated

$$H_a(T) = \tfrac{1}{2}m_aT^2 + c_aT + P \qquad 8.3.$$

$$H_g(T) = \tfrac{1}{2}m_gT^2 + c_gT + Q \qquad 8.4.$$

Where

H_a and H_g are the enthalpies for the amorphous and glassy states respectively

P and Q are integration constants

Subtracting these equations will give the enthalpy increase between two temperatures. T_1 is a temperature below, and T_2 is a temperature above the T_g.

$$\text{Enthalpy increase} = H_a(T_2) - H_g(T_1)$$

$$= \tfrac{1}{2}m_aT_2^2 + c_aT_2 + Q - \tfrac{1}{2}m_gT_1^2 - c_gT_1 - P \qquad 8.5.$$

As the enthalpy increase can be determined[153], and T_1 and T_2 are both known, equation 8.5. can be solved to determine the value of Q-P.

At the T_g, $H_a(T_a) = H_g(T_g)$, and so the equation can be rewritten

$$0 = \tfrac{1}{2}(m_a - m_g)T_g^2 + (c_a - c_g)T_g + (Q - P) \qquad 8.6.$$

The T_g can then be determined from equation 8.6 (by the computer controlling the DSC). As the equations are quadratics, two solutions are obtained, with one being meaningless (usually below zero kelvin).

8.2.3. Experimental conditions

Every four months, between 14 and 70 mg of coating (depending on the density of the paint) was examined by DSC. Approximately the same volume of paint was used for each sample. A Perkin-Elmer DSC2 was used in this study, which is of the older, temperature difference, type. In order to minimise any errors, one aluminium pan and lid was used for all seven samples, the blank run, and for the aluminium oxide calibrant. A different pan was used every four months. The blank and calibration runs were made halfway through the sample runs in order to reduce the effects of any drift.

The samples were weighed into the tared pans using a six place balance. The lid was then placed on top of the sample and pressed down in order to attempt good thermal contact with the base of the pan, and kept in place by gently deforming the sides of the pan. A steel former was used to prepare the pan for the next sample.

Each sample was placed in the DSC at room temperature, and was then cooled to 230 kelvin (-43 °C) at a rate of 20 K per minute. After a delay of 0.3 minutes, the sample was heated at 20 K per minute to 370 K (97 °C). Data were collected by the computer every two seconds (every $\frac{2}{3}$ °C).

It was found that after a run, the samples had usually partially fused together, enabling them to be removed with a pair of tweezers without contaminating the pan for the next sample. Indeed, the blank run (which was carried out either after Sample 3 or Sample 4) never showed any signs of contamination.

8.3. Dynamic Mechanical Thermal Analysis

8.3.1 Introduction

Dynamic mechanical thermal analysis (DMTA) is also referred to as dynamic mechanical analysis (DMA) the two different terms resulting from rival manufacturers. Personally, I prefer to use the former name as it reinforces the fact that mechanical properties are studied as a function of temperature.

When a material is subjected to a stress, a corresponding strain is produced. Part of this strain is elastic in that, when the stress is released, the material returns to the original form. Part of the strain is non-elastic (i.e. some energy is lost from the material), and this may result in a permanent deformation. DMTA subjects a sample to a sinusoidal stress, and measures the sinusoidal strain produced. This strain lags behind the applied stress, and this lag is also recorded (Figure 8.3.1).

The strain wave can be deconvoluted into two sinusoidal waves (Figure 8.3.2), one being in-phase with the applied stress, and the other being out-of-phase. The in-phase strain is due to the elastic component, and the out-of-phase strain is due to the viscous component. The amplitudes of these strain waves can be measured.

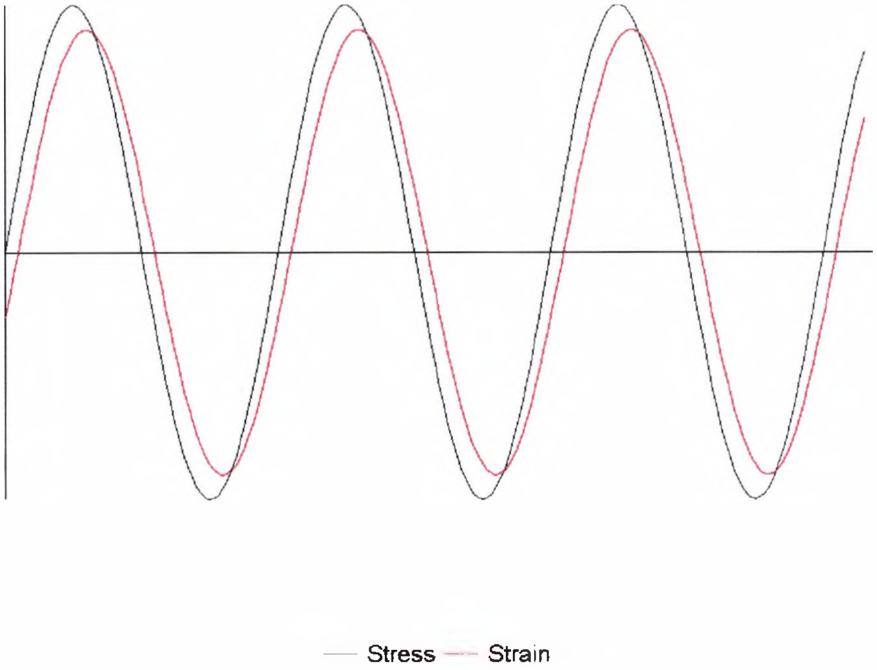


Figure 8.3.1. An applied sinusoidal stress results in a corresponding strain.

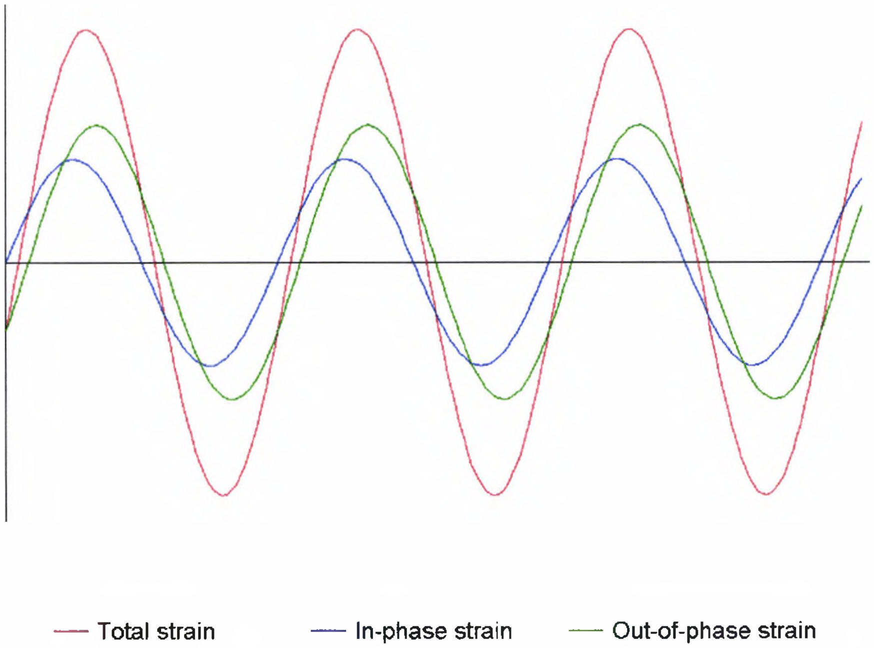


Figure 8.3.2. The strain can be deconvoluted into an in-phase strain and an out-of-phase strain (to the applied stress). The sum of the in-phase and out-of-phase strains is numerically equal to the total strain.

The ratio of the amplitude of the elastic (in-phase) strain to that of the applied stress is called the “storage modulus” (E'), and represents the proportion of the applied energy that can be recovered. This is attributed to the alteration of bond angles along the polymer chain.

The ratio between the viscous (out-of-phase) strain amplitude and the applied stress amplitude is called the “loss modulus” (E") and is due to the breaking of molecular bonds, and friction as polymer chains are forced to slide over each other.

The lag between the applied stress and the resulting total strain can be expressed as an angle termed δ. The tangent of the angle δ can also be defined as the ratio of the loss modulus to the storage modulus (i.e. $\tan \delta = E''/E'$). Tan δ is also called the loss tangent.

Below the T_g (glass transition temperature), the loss modulus (E") is relatively low, and the storage modulus (E') relatively high, thus, tan δ is small (Figure 8.3.3).

As a polymer is heated, the loss modulus (E") firstly starts to increase, causing tan δ to increase. The increase of the loss modulus is due to a high degree of friction while the polymer is being heated, but still held in the rigid, glassy, state.

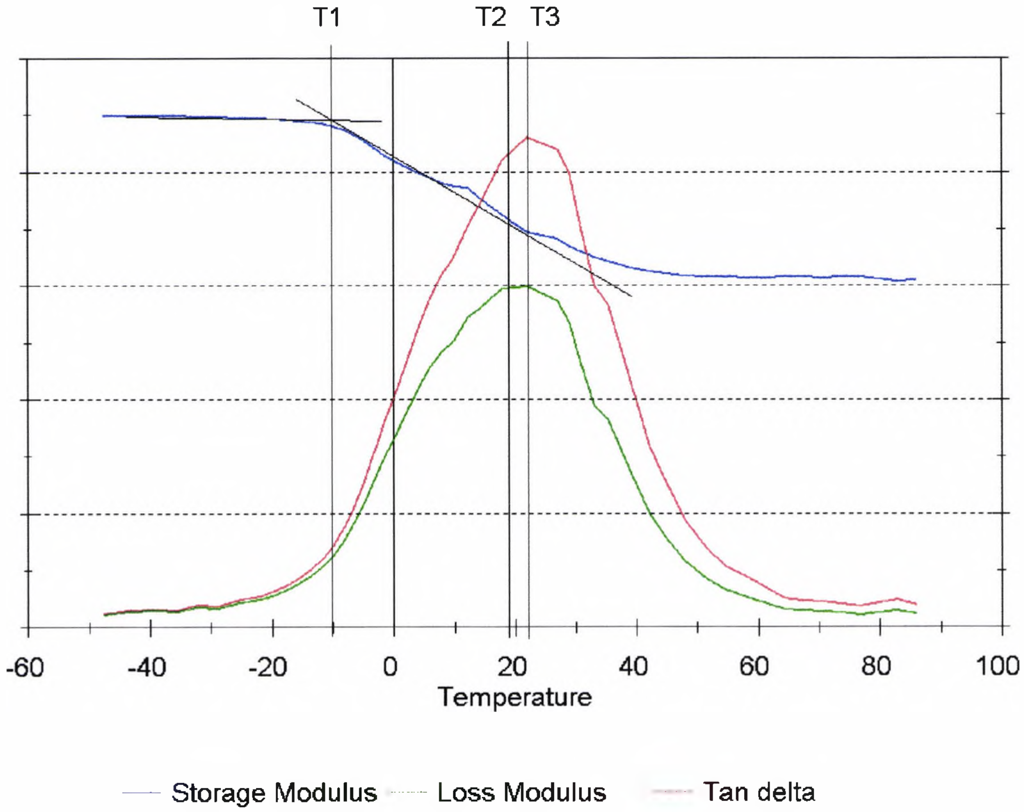


Figure 8.3.3. DMTA plot of an unexposed, unpigmented alkyd (System 1).

T1 is the "cliff-top" T_g,

T2 is the loss modulus T_g,

T3 is the tan δ T_g.

As the T_g is approached, the storage modulus (E') decreases rapidly as the bonds are given more energy and freedom, and consequently, tan δ will also increase.

After the T_g, the interaction between polymer chains decreases, and the loss modulus decreases. By this time, the storage modulus is stabilising, and so tan δ starts to fall again.

8.3.2. Interpretation of results

8.3.2.1. T_g

The maximum of this characteristic rise and fall of the value of tan δ is usually taken as the T_g [154], although the start of the decrease in the storage modulus (which measures the stiffness of the polymer) is sometimes used[155]. This "cliff-top" T_g is always less than the tan δ T_g (Figure 8.3.3). Richard[156] used the maximum value of the loss modulus as the T_g. Work by Achorne and Ferrillo[157] indicates that the average of the loss modulus maximum T_g and the tan δ T_g approximates to the T_g as determined by DSC.

The modulus of the polymer is also time dependent in that it recovers slowly from the applied stress. The values of T_g determined by DMTA are thus dependent on the frequency of the applied stress sine wave[158]. The higher the frequency, the higher the observed T_g. As a consequence of this, the T_g measured by DMTA is always higher than that determined by DSC. Achorne and Ferrillo[157] report that tan δ T_g tend to be 10 to 30 °C higher than those measured by DSC, and that DMTA T_g tend to be shifted 6 to 8 °C for every decade increase in test frequency. Bratton et al[159] also found that the T_g of coatings were also dependant on substrate type and thickness, and that even if results were extrapolated to zero thickness, the T_g of a supported film was still different to that of a free film.

A consequence of this is that DMTA determines a dynamic T_g, whereas DSC measures static T_g. Coatings applied to wood would be expected to experience relatively slow dimensional changes, and so the static T_g measured by DSC will give a better indication of the nature of the coating. The log tan δ T_g as determined by DMTA was only used to determine supplementary information, e.g. degree of plasticisation.

8.3.2.2. Cross-link density and plasticisation

For any one polymer type, as the cross-linked density increases, the storage modulus (E') increases, with the loss modulus (E") either falling or remaining constant. This will depress the maximum value of tan δ. If, however, there was an increase in the level of plasticisation, the T_g, and consequently, the tan δ peak, would occur at a lower temperature. Observing the height and temperature at which the maximum value of tan δ occurs, relative to an unexposed polymer, yields information about the chemical changes and associations occurring in the film as a result of exposure to natural weathering (Figure 8.3.4).

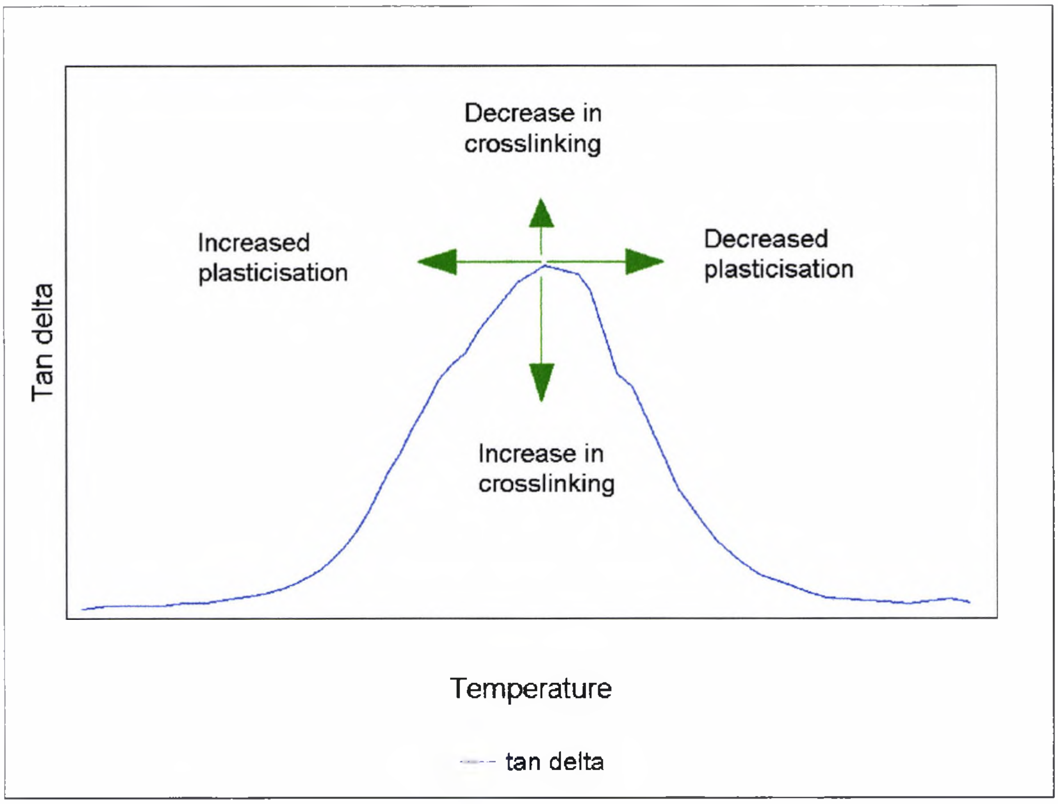


Figure 8.3.4. Plot illustrating how the shift in the maximum value of tan δ can yield information about the state of the polymer

8.3.3. Experimental conditions

The DMTA equipment used for this work was an instrument manufactured by Polymer Laboratory plc, fitted with a tensile head. One end of a detached film was attached to a stationary clamp. The other end of the film was attached to a clamp connected to a stepper motor and a sinusoidal wave generator which applies the wave in the plane of the film (Figure 8.3.5). The film was under tension so that when the film is "pushed", it did not buckle. A force of between 0.05N and 1N (dependent on the type of coating being studied and its age) was applied to pre-tension the film before the run was commenced in order to prevent buckling of the film when the sinusoidal motion was "pushing" the film. This force was chosen by trial and error, as a compromise between being too low (with the film buckling) and too high (with the film breaking). The force required was found to vary from system to system, as well as with exposure time.

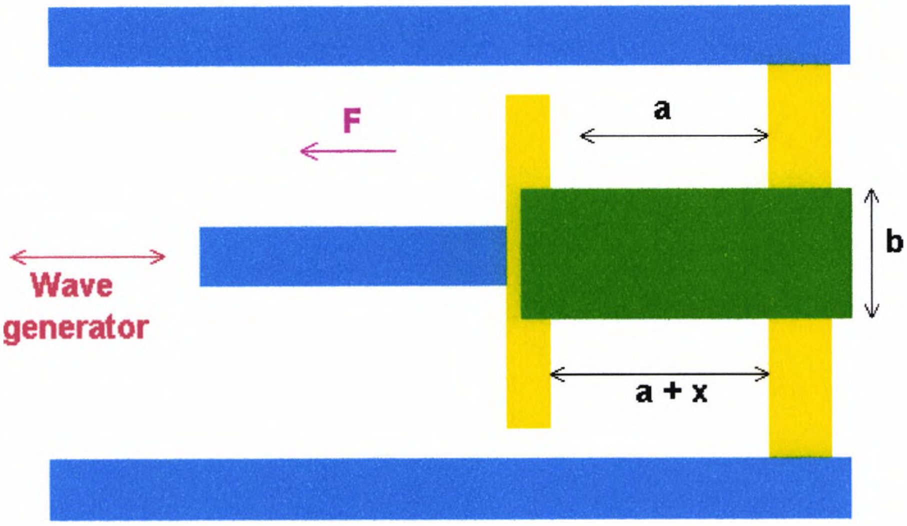


Figure 8.3.5. Schematic diagram of a DMTA tensile head. Measurements a and b are the dimensions of the polymer (shown in green) before pre-tension force F is applied, stretching the film by x. The amount of material in and beyond the clamps (shown in yellow) was assumed to have little effect on the value of the strain measured.

It was found that a film with a thickness less than 100 μm broke when a load was applied by the tensile head, because the film was too fragile. 100 μm is much less than the thicknesses intended to be used with the tensile head, but greater than the design thickness of most paint systems intended for the protection of wood. This thickness was accepted as being the best compromise between experimentally ideal thicknesses and practical paint thicknesses.

The length and width of the detached film was measured to within 0.01 mm, and the thickness to within 0.001 mm. The film thickness varied across the sample, and so an average film thickness was used. Errors of about 1% in measuring the dimensions of the film is estimated to result in an error of about 5% in the value of the log storage modulus.

The thinness of the films (in DMTA terms) and resonance at specific temperatures also gave rise to scatter in the data points for some films. Consequently, those films were studied up to six times in order that these errors were minimised. These repeats also enabled a manual smoothing technique to be employed, to reduce the effects of scatter.

It was also found that the latex based stain (System 4) could not be studied at frequencies higher than 0.1 Hz due to slow recovery times. Consequently, this frequency was used for all experiments.

8.4. Infra-red Spectroscopy

8.4.1. Fourier Transform Infra-red Spectroscopy

With conventional, dispersive, infra-red spectroscopy, infra-red light is shone through a sample. Vibrations within an inorganic or organic molecule selectively absorb some frequencies, and the emerging light is split into its component wavelengths using diffraction gratings. The filtered light is compared to a reference beam, and so a graph is generated plotting absorption as the ordinate, and wavelength (or wavenumber - reciprocal wavelength) as the abscissa. This has a disadvantage in that a scan from 4,000 to 600 wavenumbers is fairly slow, and energy is lost at the diffraction gratings (and elsewhere in the spectrometer).

Fourier transform infra-red spectroscopy overcomes these limitations by using a different optical engineering design, and a mathematical tool developed by Joseph Fourier, which relates periodicity with wavelength[160,161].

In order for Fourier analysis to take place, an interferogram must be generated. When two or more wavelengths are combined, a complex interference wave results (Figure 8.4.1.1). A beamsplitter "bounces" half the infra-red beam off a stationary mirror, and the other half off a moving mirror[162-164] (Figure 8.4.1.2).

Light from the two mirrors is recombined, when individual wavelengths will interfere constructively or destructively, depending on the position of the moving mirror at that instant in time (Figure 8.4.1.3).

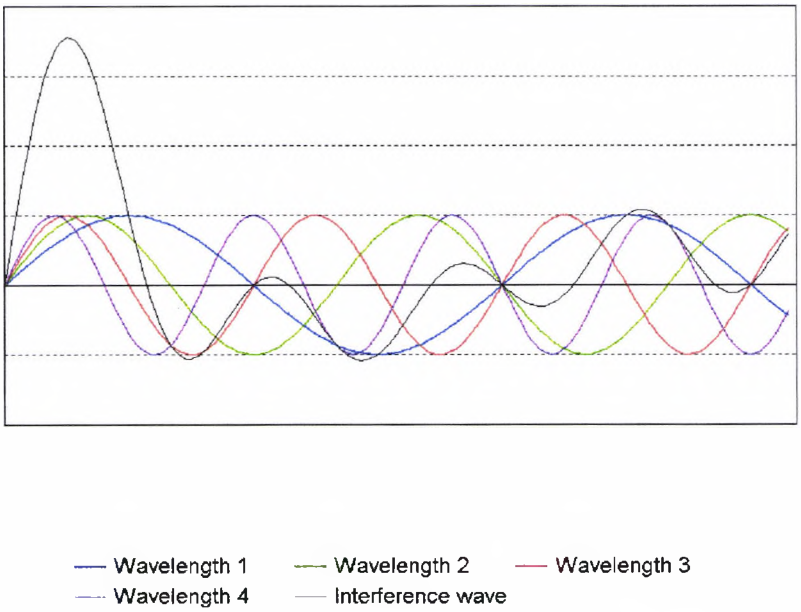


Figure 8.4.1.1. A graph showing the formation of an interference wave.

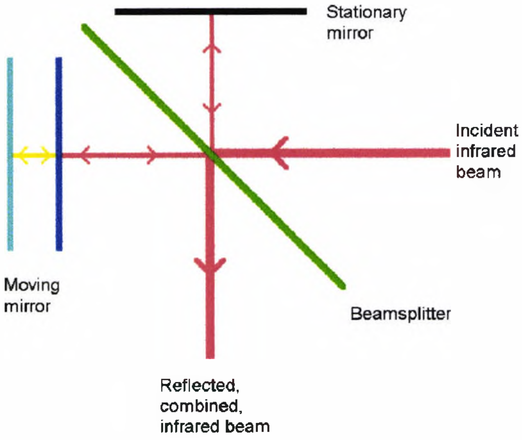


Figure 8.4.1.2. Schematic diagram of the optical arrangement. The moving mirror will cause individual wavelengths to interfere with themselves when the beam is recombined.

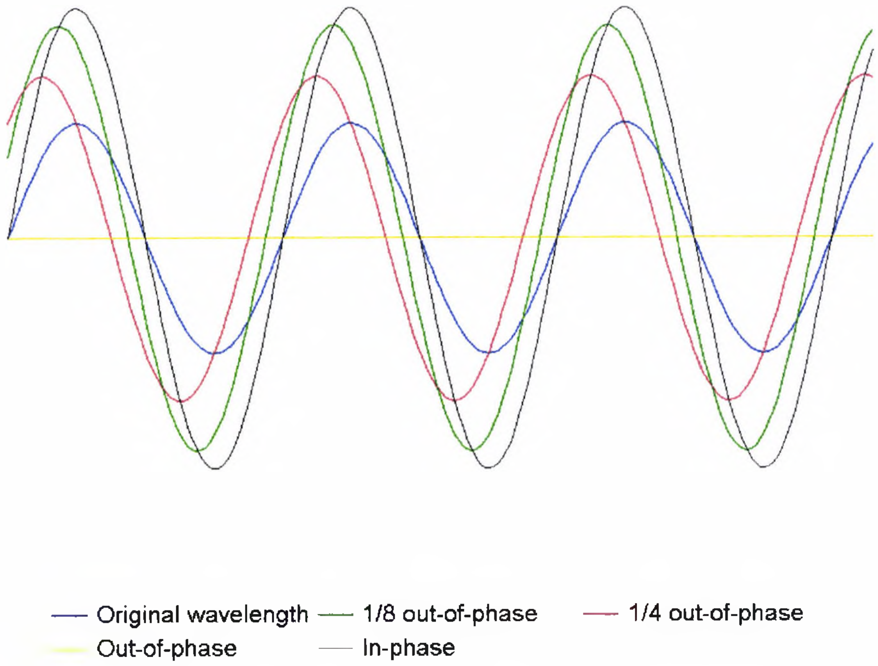


Figure 8.4.1.3. Effect of position of the moving mirror on one wavelength.

The resulting, complex, interferogram is shone through the sample. Selective wavelengths will be absorbed, and, through Fourier transform mathematics, a computer can calculate the infra-red spectrum of the sample, without having to use physical processes (i.e. diffraction gratings). Modern computing power enables spectra to be obtained very quickly, and so many spectra can be measured in a few seconds. Superimposing these spectra tends to cancel out any random noise, and improves the signal to noise ratio.

8.4.2. Photoacoustic Spectroscopy

Photoacoustic spectroscopy is a surface technique which can be used both with infra-red and ultraviolet-visible spectroscopy[163]; only the infra-red (and more specifically, FTIR) version will be discussed here.

A beam of white infra-red "light" having a range from 600 cm^{-1} to 4000 cm^{-1} is shone onto the surface of a sample in a sealed cell (Figure 8.4.2). Specific frequencies are absorbed by the sample, and warm the gas above the sample. As the cell is sealed, a pressure (sound) wave is created, and this can be recorded by a microphone inside the cell. Each frequency absorbed will have a different energy, and will therefore convert this into different sound waves. These sound waves can be deconvoluted by a computer (and appropriate software) into an infra-red spectrum of the surface.

A consequence of the differing energies of the radiation is that the depth of penetration is dependent on frequency of the moving mirror and wavelength. Falla and Smith found[165] that the depth of penetration for the equipment used here was approximately 3 μm. This depth was determined by overcoating a surface with a dissimilar polymer of varying thicknesses; the thickness of the second coating which obscured absorptions from the original surface was approximately 3 μm. This depth must therefore be regarded as an average over the spectrum, although it is acknowledged that wavenumber 600 cm^{-1} will penetrate deeper than 4000 cm^{-1}.

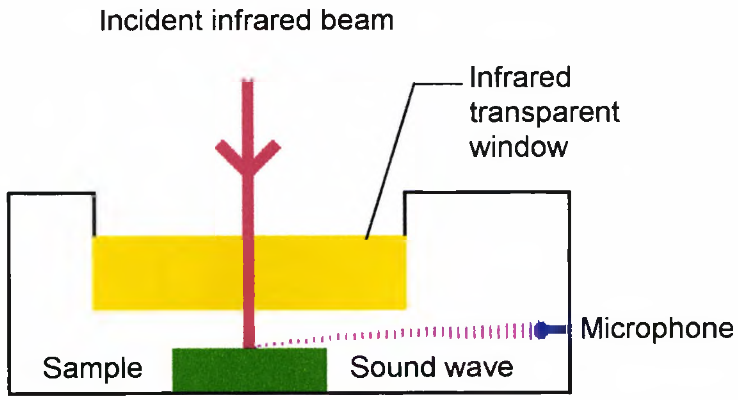


Figure 8.4.2. Schematic diagram of an infra-red photoacoustic cell

As with other forms of infra-red spectroscopy, the detection limit depends on both the functional group (the strength of the absorption) and the matrix (whether such an absorption would be masked). Additionally, in photoacoustic spectroscopy, the gap between the top of the sample and the bottom of the cell window is critical, and the optimum size for the gap is again frequency dependent. The smaller the gap, the greater the pressure and hence the sound wave (and resulting infra-red spectrum). However, if the gap is too small, the longer wavelength radiation is damped out, resulting in a reduced peak absorption intensity. Consequently, it can be dangerous to quantify changes when the reference and quantified peak are not immediately adjacent.

8.4.3. Experimental conditions used for FTIR-PAS

A Bio-Rad FTS-40 infra-red spectrometer was set up with the following conditions as default:

Mirror speed	5 kHz
Number of scans	256
Resolution	16

Wooden panels (Section 7.2.) were studied by Fourier Transform Infra-Red photoacoustic spectroscopy. As with other experiments, measurements were made every four months of natural exposure and each system was studied in duplicate.

It was found that water retained in the wood came out during analysis, fogging the cell window. Accordingly, portions of the samples were cut from the panels, dried by heating them at 105 °C for at least eight hours, and allowed to cool over phosphorous pentoxide in a dessicator. This conditioning could affect the samples, for example, by thermal degradation.

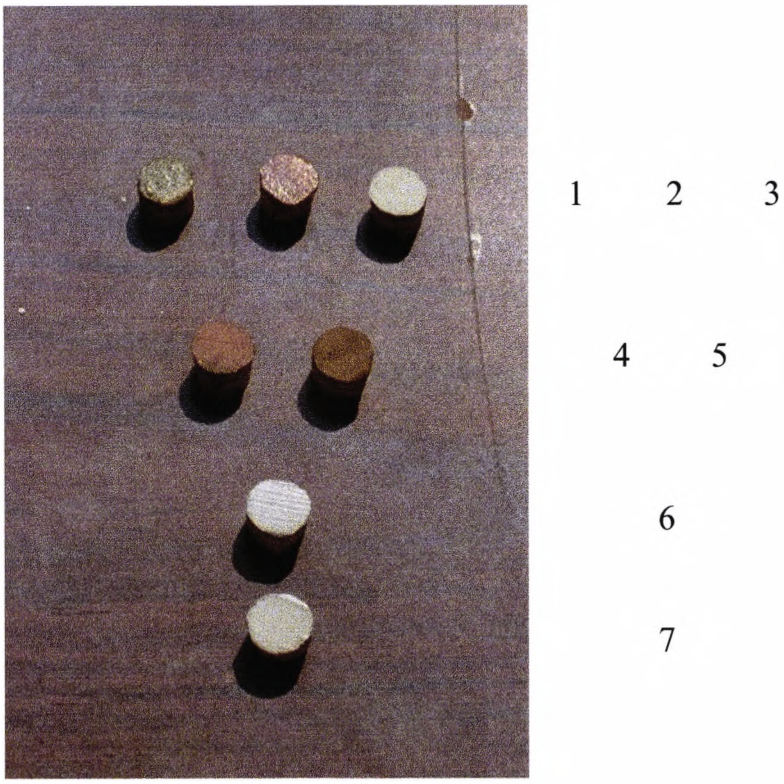


Figure 8.4.3. Blocks (shown actual size) for FTIR-PAS analysis. On the top row, from left to right, are Systems 1 to 3, next Systems 4 & 5, then System 6, and finally System 7 (see Sections 6.2. to 6.4. for the descriptions of each system)

Samples 9 mm in diameter (to fit the photoacoustic cell) were cut using a scalpel. Some error in height, flatness, and surface area is to be expected due to the grain of the wood (Figure 8.4.3). In spite of these possible errors, any major chemical change of the surface of the paint will be shown as changes in the infra-red spectra.

8.5. Determination of low molecular weight plasticisers

8.5.1 Introduction

The volatile content was determined in order to measure the quantity of low molecular weight plasticisers present. Strictly speaking, heating a sample cannot be used to determine the volatile content of coatings, as even gentle heating has been found to degrade certain resins. The technique does, however, determine the fraction which is neither volatile nor degraded. For this study, thermal degradation was assumed to be negligible.

Plasticisers decrease the observed T_g. Experimental work has shown that alkyds continually form autoxidation products which are, to a greater or lesser degree, trapped in the film. While acrylics do not exhibit this phenomenon, they will also be affected by plasticising components, possibly as a result of degradation. Analysis for plasticising components was therefore carried out in order to help explain any changes in the T_g measured by DSC (Section 8.2.).

8.5.2. Experimental conditions

Aluminium panels were withdrawn every four months of natural exposure and a portion of each film was removed, and tested to BS 3900 part B2 (1981). Essentially, a sample was heated at 105 °C for three hours in a fan assisted oven, and allowed to cool in a dessicator dried by phosphorous pentoxide.

Owing to the limited amount of sample available, the test portion was scaled down by between 20 and 50 times (depending on the density of the film) from that in the Standard, and the weight losses measured to 0.001 mg instead of 1 mg using a Sartorius six place microbalance.

Further deviations from the Standard were made, in that dried paint scrapings were used instead of liquid paint, and that small porcelain crucibles were used instead of flat dishes. The use of flat dishes as required in the standard is in order to provide the liquid paint with a large surface area from which volatiles escape. Paint scrapings do not, as a rule, pack very well, and, as they have a surface both sides, a large surface area was maintained. The relatively high sides of crucibles also helped minimise sample losses due to air currents generated by the oven fan.

While this Standard is intended to determine the portion of non-volatile matter in a liquid paint (i.e. the proportion of solvent etc. to solid components, e.g. resin and pigment), it will also determine the quantity (but not the nature) of any volatile plasticisers.

An attempt was made to study the nature of the volatile portion using gas chromatography/mass spectrometry (GC/MS), by injecting a portion of the film into a heated chamber with a quartz wool filter, and a stream of helium supplying the GC column. Unfortunately no real results were obtained. This may have been due to the components being below the detection limit of the mass spectrometer, and/or that the chromatographic conditions used prevented them from passing through the column. It was not reasonable to pursue the analysis of the volatile components, which could only be a very minor part of the whole project.

8.6. Determination of polar non-volatile material

The proportion of polar non-volatile material was determined by a water extraction method. Such material (e.g. aldehydes, alcohols, thickeners, defoamers) could plasticise the coating.

Water extraction was carried out according to BS 3483 part C2 (1979), equivalent to ISO 787/8, which was designed to study the water extractable content of pigments, with the exception that the sample weight and volume of water were both reduced by a factor of ten. This technique uses water distilled twice, to which ethanol is added at a concentration of 5% v/v to act as a wetting agent.

Between 0.2 and 2 g of paint film, depending on the density of the paint, (weighed to the nearest 0.01 mg using a Mettler five place balance), was placed in a beaker, and 20 ml of the water/ethanol mixture was added. The beaker was agitated using an orbital stirrer for one hour at room temperature, and then filtered quantitatively using a 0.2 μm filter into tared 75 mm by 25 mm vials. The extract was evaporated first using a steam bath, with a stream of nitrogen to aid evaporation, and finally in an oven at 105 °C for 30 minutes. The vials were allowed to cool in a dessicator dried by phosphorous pentoxide, before being weighed, again using the Mettler five place balance.

An attempt was made, by H. D. Mehta and K. E. Walker, to study the nature of the extracts by high pressure liquid chromatography and infra-red spectroscopy, but their results, unfortunately, proved inconclusive.

8.7. Determination of non-polar non-volatile material

The proportion of dichloromethane extractable material was determined in order to ascertain the presence of non-polar non-volatile plasticisers (liquid dichloromethane having a dielectric constant[166] of 9 at 20 °C as opposed to liquid water's[167] 80 at 20 °C).

A Soxhlet technique was used for the dichloromethane extraction. This was based on BS 4325 part 5 (1978) which describes the extraction of oil seeds by diethyl ether. The extraction was carried out for six hours, such that the drops from the condenser fell at a rate of two to three per second. The temperature of the extraction was not measured, but previous work at the Paint Research Association suggests that it is approximately two thirds of the boiling temperature, in this case about 25 °C.

Between 0.2 and 2 g of paint (depending on the density of the coating) was used for this determination. It was found that the flakes of coating could be encapsulated by being wrapped in Whatman 542 filter paper. When this method was employed, the fragments were prevented from being carried into the round bottomed flask, while the porous nature of the filter paper allowed them to be wetted by the dichloromethane. Conventional Soxhlet thimbles allowed some of the sample (in particular pigment freed from the binder as the resin swelled) to be carried over.

After extraction, the greater part of the dichloromethane was removed by distillation, and the remainder made up to 10 ml. 5 ml was evaporated on a steam bath, using a stream of nitrogen to reduce oxidation, and finally in a vacuum oven at 75 °C for ninety minutes. Extracts were stored in a dessicator over phosphorous pentoxide until cool, and then weighed to 0.01 mg using a Mettler five place balance.

The second 5 ml portion was removed for analysis by high pressure liquid chromatography (work carried out at PRA by H. D. Mehta and K. E. Walker). Unfortunately, these attempts to identify the nature of the extracts again yielded inconclusive results.

8.8. Organic content

This was carried out to enable the amount of extractable material to be expressed as a percentage of the resin content. It would also illustrate major changes in the pigment volume concentration with time (due to erosion of the resin).

The analysis was carried out to a standard PRA ashing method, which involves heating the sample, in a porcelain crucible, from 100 °C to 250 °C at a rate of 2 °C min^{-1}, keeping at 250 °C for one hour, and then increasing the temperature to 450 °C, again at 2 °C min^{-1}. The sample was maintained at 450 °C for sixteen hours before being transferred to a dessicator over phosphorous pentoxide. When the samples had attained room temperature, they were weighed to the nearest 0.001 mg using a Sartorius six place microbalance.

9. Results

9.1. Introduction

The results obtained will be considered in three parts: the initial values of T_g, storage modulus, etc.; the effect of natural weathering on these values; and infra-red spectra. The infra-red spectroscopy technique used only analysed the surface, whereas all the other techniques studied the bulk of the film, and that is why it is treated separately.

As alkyd and acrylic resins are expected to undergo different chemical reactions, a further subdivision will be made in order to consider each resin type in turn.

Unlike panels reserved for other experiments, the exposure of all films used for dynamic mechanical thermal analysis (DMTA) began in December (four months after the main set of panels). In all cases, panels were exposed for twenty-four months, and examined every four months during that period.

The four techniques

- determination of volatile material
- determination of polar non-volatile material
- determination of non-polar non-volatile material
- changes in the pigment volume concentration

did not show significant changes during the exposure period, and so the results are not presented in full. Table 9.1 shows the results for the traditional three coat alkyd, System 7, before and after twenty-four months exposure. The other systems underwent similar changes with time.

Table 9.1. Typical results for System 7, the traditional, three coat, alkyd

Exposure time (months)	% w/w of volatile matter	%w/w of polar non-volatile material	%w/w of non-polar non-volatile material	% w/w of organic content
Unexposed	1	2	11	45
Twenty-four	2	3	8	43

9.2. Initial values

9.2.1. Alkyds

Three of the coatings (Systems 1, 2 and 3) were based on the same alkyd resin and the same driers, merely having different pigmentation (Section 6.2.1.). The fourth coating (System 7) was based on a different, traditional alkyd resin (Section 6.2.2.). As T_g (glass transition temperatures) measure changes in the organic component of the coatings, a cursory assessment would be that Systems 1, 2 and 3 should have the same initial T_g, and System 7 a different initial T_g.

Table 9.2.1. Initial T_g, determined by DSC.

The uncertainty is thought to be ±1°C.

	Description	Temperature in °C
System 1	Unpigmented flexible alkyd resin	12
System 2	Brown, semi-transparent, flexible alkyd resin	8
System 3	White, opaque, flexible alkyd resin	13
System 7	White, opaque, traditional alkyd resin	24

Examination of Table 9.2.1 shows that Systems 1 and 3 do indeed have a similar T_g. System 2, the flexible alkyd formulated with semi-transparent iron oxide as a stain, however has a much lower T_g than all of the other alkyds. While the differences between Systems 1, 2, and 3 might be acceptable if the systems were studied by different techniques (Section 8.2), the fact that there is such a large difference within one technique is significant.

Figure 9.2.1 shows the DMTA results for the unexposed alkyd resins. The plot of the log of the storage modulus (log E') is similar for both System 1 (the unpigmented flexible alkyd) and for System 2 (the brown, semi-transparent, flexible alkyd).

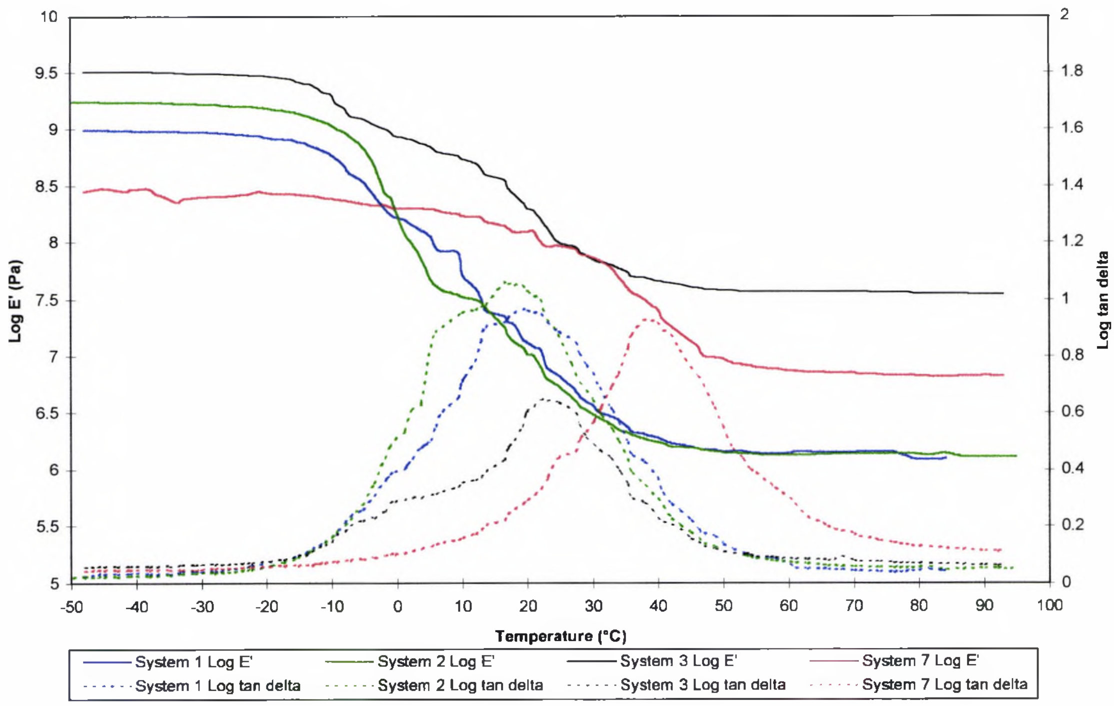


Figure 9.2.1. DMTA plots of the unexposed coatings based on alkyd resins.

The maximum value for log tan δ for System 2 is higher in magnitude and at a lower temperature than that for System 1, indicating that System 2 is more plasticised and less cross-linked than System 1, which together could partially explain the depression in glass transition temperature as measured by DSC. The reason for this depression will be discussed below (Section 9.2.1.1).

For System 3 (the white, opaque, flexible alkyd) there is less organic material, and this accounts for the lower maximum value of log tan δ. An interesting effect of this increase in pigmentation is that the value for the storage modulus is much higher, above the glass transition temperature for System 3 than either System 1 or System 2. As the storage modulus is proportional to the elastic component of the coating (Section 8.3), the stiffer the coating, the higher the value for log E'. Thus, the addition of pigment makes the film much stiffer above the glass transition temperature. This "reinforcing" effect will also tend to lower the maximum value of log tan δ.

With System 7 (the white, opaque, three coat traditional alkyd), the storage modulus is lower than the other systems below the glass transition temperature, indicating that, when the free volume of these systems is reduced, the traditional resin is more flexible. Above the glass transition temperature, however, the flexibility is less than that of System 3 (the flexible analogue).

It may be tempting to look at the position of the maximum value of log tan δ in order to judge whether System 7 is more or less crosslinked, or more or less plasticised, than System 3. This would lead to erroneous conclusions, as the two resins are different enough (Section 4.1.1.1) to render such comparisons invalid.

9.2.1.1. Lowering of T_g

In order to explain why System 2 has a lower T_g than Systems 1 and 3, we must compare their formulations (Section 6.2.1). System 1 had no pigment, System 3 has the same organic materials as System 1, but with titanium dioxide. System 2 used a pigment dispersion to incorporate iron oxide. This pigment dispersion used an alkyd resin based on linseed oil.

There are three possible reasons for the depression of the T_g:

1. the linseed oil alkyd in the pigment dispersion is lowering the T_g of the coating
2. the iron oxide pigment is responsible for the change
3. both linseed oil and iron oxide contribute (whether synergistically or not) to the lowering of the T_g

9.2.1.1.1. Lowering of T_g by organic content

In order to determine whether the linseed alkyd was solely responsible for lowering the T_g of System 2, a sample of Sicoflush Yellow 1916 C4 was prepared with the same drier percentages as was used in System 2 (namely, 0.06% cobalt, 0.09% zirconium and 0.12% calcium). A film of this sample was cast onto a glass panel, and allowed to dry for at least 14 days, after which, its T_g was measured in the same way as System 2.

It is acknowledged that in the coating, the Sicoflush Yellow 1916 C4 would be dried by a lower concentration of driers, as some of the driers would be used to dry the main binder as well. It was assumed that the linseed oil alkyd in Sicoflush Yellow 1916 C4 would have the same access to the driers in System 2 as the other resins, and therefore it should be dried using the same concentration of driers.

It was found that the T_g of Sicoflush Yellow 1916 C4 was -3°C. It is clear that the linseed oil alkyd will affect the T_g of System 2, the extent of which can be calculated according to the method used by Schmid[151], using the T_g of System 1 as the T_g of the main binder.

$$1/T_{g(\text{calculated})} = w_{(a)}/T_{g(a)} + w_{(b)}/T_{g(b)}$$

where

T_g is the glass transition temperature in kelvin

w is the weight proportion of components a and b

$$1/T_{g(\text{calculated})} = (0.6883+0.2130)/285 + 0.0987/270$$

$$= 0.00316 + 0.00037 = 0.00353$$

$$T_{g(\text{calculated})} = 283 \text{ kelvin } (10\ °\text{C})$$

for comparison

$$T_g \text{ (System 1)} = 285 \text{ kelvin } (12\ °\text{C})$$

and

$$T_g \text{ (System 2)} = 281 \text{ kelvin } (8\ °\text{C})$$

Thus, the linseed oil alkyd is only directly responsible for a suppression of 2 °C, whereas the actual suppression is 4 °C. The experimental error for determining the T_g is thought to be less than 1 degree, and so the extra 2 degree drop in T_g must be due to another mechanism.

9.2.1.1.2. Lowering of T_g by inorganic content

The second hypothesis is that the iron oxide pigment is itself altering the T_g. The effect of "fillers" on the glass transition of polymers has been studied. Sato[168] found that the T_g of a variety of polymers (including acrylics, alkyds, epoxy resins and synthetic rubbers) could either increase, or stay the same after various fillers were incorporated. This effect was attributed to a "modulus reinforcing theory". Howard and Shanks[169] postulated that fillers would increase the T_g of a polymer if that polymer were absorbed onto the surface of the filler.

Peyser and Bascom[170] found that the thermal history of the sample could change both the magnitude, and even the sign of the change in T_g due to the "filler effect". Peyser[171] later found that thermal stresses could only account for small changes in T_g, but was reluctant to suggest a primary explanation.

Pigments could change the T_g either by a physical process (the "modulus reinforcing theory"), or a chemical process (not discussed by the above authors). The possibility that both processes apply should not be overlooked.

9.2.1.1.2.1. Physical Processes

As a resin goes through its T_g, physical properties change disproportionately (Section 8.2); this includes dimensional changes. As each pigment particle has to be coated ("wetted") by the resin, a disproportionate dimensional change at the surface of the pigment will result. If the resin is able to form strong bonds with the pigment (e.g. co-ordination bonds akin to chelating agents, hydrogen bonding, or ion pairs), there will be a resistance to dimensional change, which will result in a shift in the observed T_g. This effect will be peculiar to both the resin and the pigment, but the magnitude of the shift will be dependent on the concentration of pigment, and also the surface area. Thangavel, Subbi Reddy, and Yaseen[172] found that interactions were formed between iron oxide and an alkyd resin solution, but earlier work by Shareef and Yaseen[173] indicated that this interaction could be solely between iron oxide and solvent.

As the surface area of the semi-transparent iron oxide will be large (and greater than the surface area of pigments used for opaque coatings), a shift in the T_g of up to 4°C may be reasonable. As functional groups in alkyds are expected to be similar (Section 5.3), such an interaction would be expected to affect the measured value of the T_g, determined for Sicoflush Yellow 1916 C4. In that case, the interactions would be expected to be greater due to the higher concentration of iron oxide in the linseed oil alkyd. This hypothesis, if true, would render the calculations in Section 9.2.1.1.1 invalid.

If the iron oxide particles were affecting the free motion of the resin molecules, there would be an increase in the storage modulus, and a suppression in the maximum value of tan δ (due to the composite being effectively more crosslinked). Both of these are seen in Figure 9.2.1, but the increase in storage modulus is thought to be within experimental error.

9.2.1.1.2.2 Chemical Process

The other possibility is that iron oxide affects the crosslinking mechanisms to form a lower molecular weight polymer. In the DMTA log tan δ plot, the maximum is shifted to a lower temperature and a higher value than that for a film without iron oxide. This implies that iron oxide can modify the autoxidation reactions, forming a less highly crosslinked and more highly plasticised structure on drying.

It is already known[53] that small concentrations of metals in solution affect specific autoxidation reactions, and so it is not unreasonable to assume that similar reactions could take place at the surface of solid particles. Even so, the very finely divided semi transparent pigment would have considerably less effective surface area than a metal in solution, but the concentration of the iron oxide is higher (at about 10%w/w of the solids content of the coating).

Such an influence on the drying mechanism would also affect the observed T_g for Sicoflush Yellow 1916 C4, but whether or not the linseed oil alkyd would be affected more than the other alkyds, would depend on the role of iron oxide (if any) on the mechanism (i.e. as a catalyst or as a concentration dependent reagent).

9.2.2. Acrylics

The similarity between the T_g of the unexposed Systems 4 (5°C) and 5 (6°C) indicates that there is little, if any, interaction between the pigment and binder. While iron oxide (which had such a dramatic effect on the T_g of the flexible alkyd - Section 9.1.1.1) is present in both System 4 and System 5, it is present at very different concentrations (3 and 16% respectively), and so, if there were an interaction, the initial T_g of Systems 4 and 5 would be expected to be different.

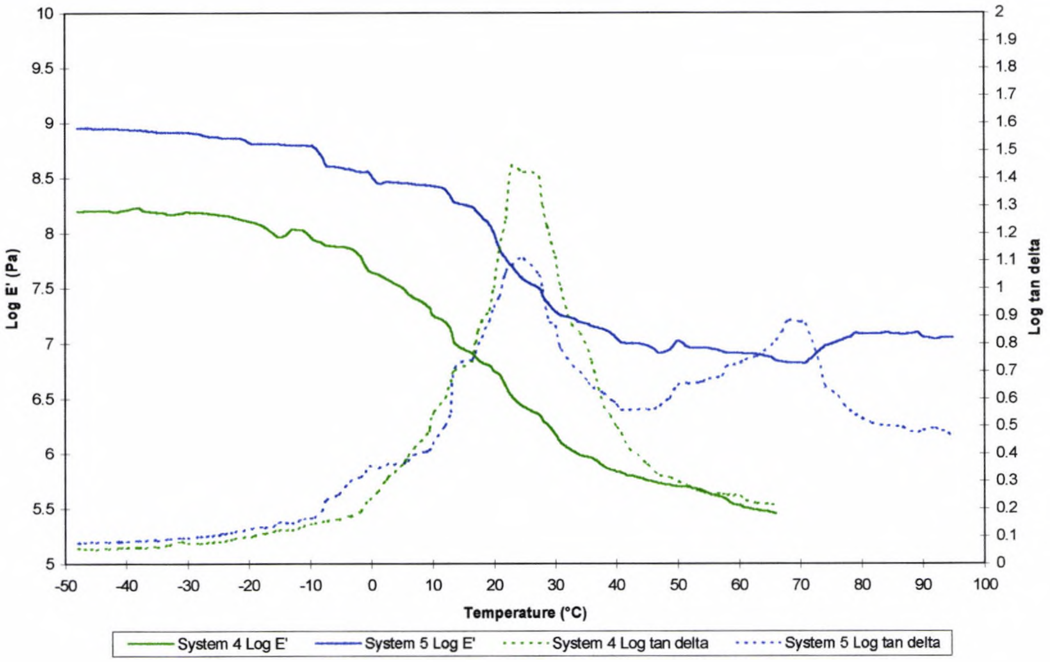


Figure 9.2.2.1. DMTA plots of the unexposed coatings based on acrylic resins.

Figure 9.2.2 shows the DMTA plots for the unexposed acrylics. The results for System 4 (the waterborne coating based on an acrylic resin, and formulated as a stain with iron oxide) cease at 65 °C. This was the point at which the coating softened to such a degree that it could not be measured as a detached film.

Although based on the same resin as System 4, the results for System 5 (the waterborne coating based on an acrylic resin, formulated as a brown opaque paint) appear to be very different. As for System 3 (Section 9.2.1.1), the drop in value for the log tan δ peak for System 5 (when compared to that of System 4) can be attributed to the increase in pigmentation. Unlike System 3, the log of the storage modulus is increased both above and below the glass transition temperature, indicating that the "reinforcing effect" is more dependent on the pigments used in System 5 (mica and iron oxide) than in System 3 (titanium dioxide and calcium magnesium carbonate) despite the pigment concentrations being similar (52% for System 5 and 60% for System 3; as determined by ashing).

Another interesting feature of System 5 is that a plot of log tan δ has two peaks, one at the same temperature as that for System 4, and the other at about 65 °C. The second peak can be explained as the temperature at which the resin "melts", causing a temporary increase in the loss component in much the same way as when the coating passes through the glass transition temperature (as explained in Section 8.2).

9.2.3. Alkyd-Acrylic Hybrid

Only one alkyd-acrylic hybrid was studied, and it was based on a mixture of a water borne alkyd and a water borne acrylic, formulated as a white paint with titanium dioxide pigment. This hybrid was labelled System 6, and has an initial T_g of 7 °C, as determined by DSC. An interesting observation is that, for the unexposed coating (shown in Figure 9.2.3), there are two peaks in the log tan δ curve, one at about 5 °C, and the other, broader peak, between 20 and 50 °C. These are due to the individual resins, which were not run independently,

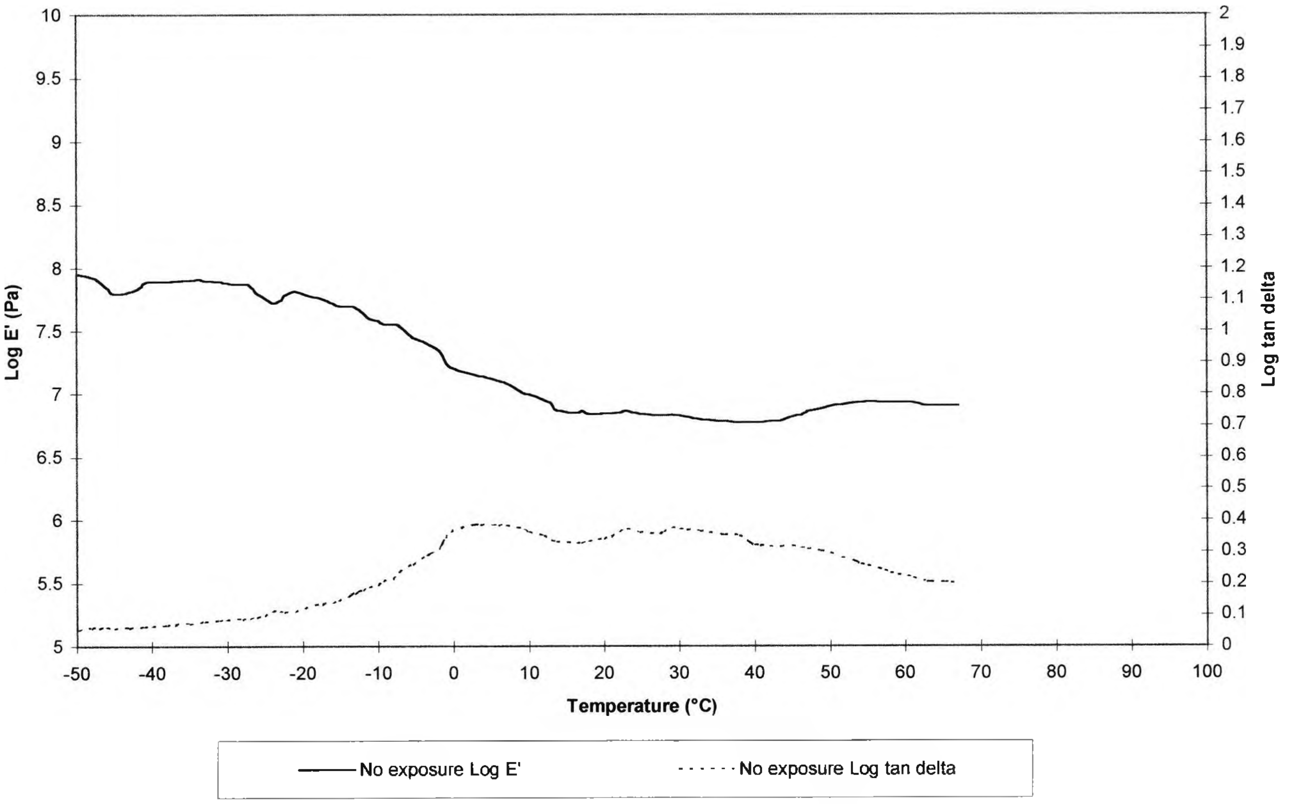


Figure 9.2.3. DMTA plot of the unexposed coating based on the alkyd-acrylic hybrid resin.

9.3. The effect of natural weathering

9.3.1. Alkyds

It will be interesting to firstly examine, fairly superficially, the alkyds in general, in terms of the effect of pigmentation and type of alkyd. Each system in turn can then be studied in more detail.

9.3.1.1. Alkyds generally

Table 9.3.1.1 shows the effect of natural weathering on the T_g. Some explanation for the changes in T_g may be gleaned from analysis of the results in a graphical format (Figure 9.3.1.1), where the T_g is plotted against the month it was withdrawn.

All of the alkyds studied showed an initial increase in the values of their T_g. This is almost certainly due to additional cross-linking reactions being promoted by the hot, high solar energy, late summer months. Effectively this implies that chromophores in the polymer backbone absorb UV light, initialising the formation of radicals. In this case, the predominant reaction is embrittlement as two long chain radicals terminate, increasing the molecular weight.

Table 9.3.1.1. The effect of natural weathering on the T_g of alkyds, as determined by DSC. The uncertainty is thought to be ±1 °C.

	System 1	System 2	System 3	System 7
No exposure	12 °C	8 °C	13 °C	24 °C
4 months	23 °C	12 °C	25 °C	30 °C
8 months	25 °C	12 °C	25 °C	34 °C
12 months	33 °C	14 °C	25 °C	34 °C
16 months	35 °C	14 °C	29 °C	34 °C
20 months	37 °C	11 °C	25 °C	33 °C
24 months	41 °C	11 °C	25 °C	30 °C

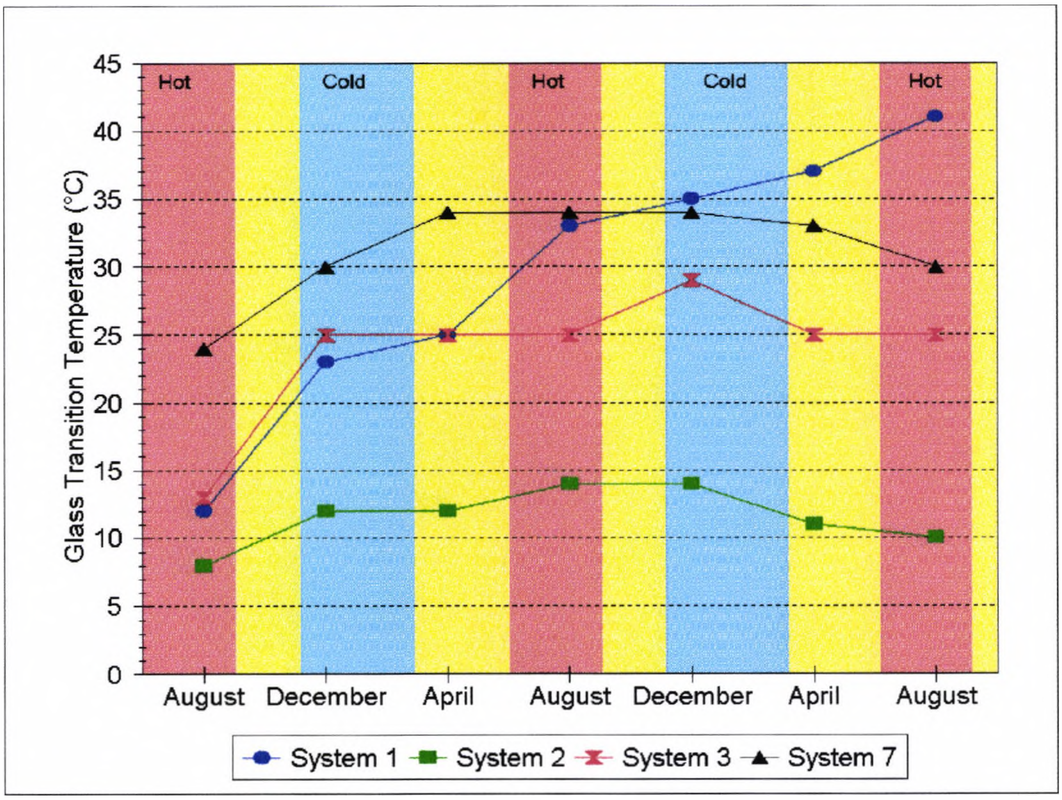


Figure 9.3.1.1. Variation of T_g of alkyds with month of measurement.

By the time of the eight month old samples, withdrawn in April, most of these additional cross-linking reactions have apparently been completed. Examination of Figure 9.3.1.1, however, shows us that these samples have only just passed the cold, weak solar energy, winter months, and so fewer radicals would be expected to be formed. It is surprising that System 1 (the unpigmented flexible alkyd) and System 7 (the white opaque conventional three coat alkyd) are different from the others with T_g continuing to rise.

System 1 is totally unprotected from ultra-violet radiation, and so even the weak, winter, solar energy could be sufficient to excite sufficient radicals to promote embrittlement. Systems 2 (the same resins as System 1, but with semi-transparent iron oxide pigment) and 3 (the same resins as System 1, but with opaque white pigmentation) could have sufficient UV absorbers (i.e. the pigment) to prevent attack.

The increase in T_g for System 7, the control system, is more difficult to explain, but it could be due to either the different resin being more susceptible, or the comparatively low pigment volume concentration in the topcoat (to increase the initial gloss), or a combination of those two factors.

All the alkyd resins have an linoleic oil type, with a length of 65% w/w, and the only disclosed difference is the type of polyol. Assuming that there are no other differences between the resins, the polyol would not have been expected to have such a dramatic effect on the UV susceptibility.

The topcoat of System 7, however, only has 32% w/w of pigment in the dried film, whereas System 3 has 43% w/w. Clearly, for System 7, there is a reduced degree of protection in the surface layer. Titanium dioxide can only protect resin and a wood substrate if it absorbs damaging light. If a topcoat, having a resin content of 68% w/w and hence less pigment, forms radicals, the titanium dioxide, in theory, would be powerless to stop them migrating to the undercoat, or even the primer.

By the following August, after twelve months exposure, the unprotected System 1 has embrittled still further, as evidenced by the dramatic increase of its T_g. System 2, being protected by iron oxide, embrittles, but not to the same extent as System 1. The T_g of the white paints, Systems 3 and 7, do not change. This could be due to either the titanium dioxide pigment reflecting/absorbing the early summer sunlight, or competing embrittlement and degradation reactions, or both. As System 7 has been shown to be susceptible to UV light, it is likely that an equilibrium between embrittlement and degradation is the main reason for the stabilisation in T_g.

During the late summer, autumn and early winter months (after sixteen months exposure), System 1 continues to embrittle. The decreased solar energy over this period accounts for the rather modest increase in the T_g. With System 2, the embrittlement and chain shortening reactions appear to be in equilibrium, possibly due to the iron oxide pigment absorbing UV radiation.

An unexpected result is that the white, opaque, flexible alkyd, System 3, experiences an elevation of its T_g over this period. This does not appear to be due to the photochemistry of titanium dioxide (Section 5.5.2), because System 7, the white, opaque, conventional alkyd does not have a corresponding increase in T_g.

While the unprotected flexible alkyd, System 1, does show that further embrittlement is possible over this period, the increase in T_g is greater for System 3, and, if this effect were due to the resin, System 1 would be expected to have the larger increase.

One might be tempted to discount this result for System 3 as being a rogue point, were it not for the fact that this method, on this type of sample, has an error of only 1 °C. Unfortunately, the determination could not be repeated due to lack of sample. While DSC is usually considered a non-destructive technique, it could not be assumed that paint would be unchanged during the determination. The sample was heated from -43 °C to 97 °C, which could change the sample (for example by "boiling off" plasticisers), and so the same portion could not be used twice.

By the following spring, month 20, System 1 has continued to embrittle. This is contrasted by the fact that all the other alkyds experienced a drop in their T_g. There are two (not necessarily mutually exclusive) possible causes for a decrease in T_g, one being that there is a reduction in molecular weight, and the other being an increase in the level of plasticisers.

A reduction in molecular weight, whether due to photodegradation of the resin, or photochemistry involving the pigment would not be expected, due to the weak solar energy. If plasticisation was the cause, the T_g of System 1 might also be expected to fall.

One possible explanation is that the pigment is somehow entrapping plasticisation agents, possibly by chelation. Another explanation is that System 1 has, indeed, been plasticised to the same extent as the other alkyd based paints, but that embrittlement reactions mask this. Determination for volatile and non-polar non-volatile plasticisers showed that these did not change significantly over the exposure period. There was, however, an increase in polar non-volatile extractable material for twenty month old System 2, from 1-2% to 6% (expressed as a percentage by weight of the organic portion of the paint). As there was not a corresponding increase for System 3, there is an implication that either pigments do not entrap plasticisers, or that they are so tightly bound that they cannot be leached by water at ambient temperature. Indeed, since the extractable material did not increase for System 1 either, it is unlikely that plasticising material was present in the coatings at this stage of their life. The high polar material content for system 2 could be explained as either reactions initiated by the iron oxide pigment, or chance contamination (being exposed outside, there was no control over what they were subjected to, e.g. bird droppings).

In the summer, after two years natural exposure, the T_g of the unpigmented flexible alkyd, System 1, has continued to rise (Figure 9.3.1.1), indicating that embrittlement (radical cross-linking) reactions are predominant over degradation reactions. The T_g of the white pigmented analogue, System 3, does not change. This implies that, at this stage in the System 3's life, embrittlement occurs at the same rate as degradation, and/or the white pigmentation is absorbing or reflecting damaging UV light.

Systems 2 and 7, (the flexible alkyd formulated with semi-transparent iron oxide, and the traditional white opaque alkyd) both experience continuing reduction in their T_g, indicating either that their overall molecular weights are falling, or that they are being increasingly plasticised, or both. Neither the volatile nor non-volatile extractable material increased, indicating that the coatings were not being plasticised.

More information about which of these mechanisms is more prevalent can be gleaned from the DMTA results, which will now be discussed for each of the systems in turn.

9.3.1.2. System 1

System 1 is a clear, unpigmented coating based on a modern flexible alkyd resin. Examination of Figures 9.3.1.2.a and 9.3.1.2.b, showing the effect of up to twenty-four months natural exposure, shows that until twenty months, the value of the log of the storage modulus below the glass transition temperature is approximately constant. The slight variations probably reflect the effect of errors incurred in measuring the dimensions of the coating (which are used to calculate the value of the modulus). By twenty-four months exposure, log E' has jumped dramatically.

More dramatic changes occur in the values of the log of the storage modulus above the T_g, when the coating is in the rubbery state. Here, the value jumps from 6.2 Pa for the unexposed film, to about 6.5 Pa after only four months, and continues to rise, to a value of about 7.4 Pa after two years.

Examination of the shift in maximum value of the log tan δ plot explains why this stiffening occurs. The maximum log tan δ point is shifted down and to a higher temperature, indicating that the stiffness increases are due to both loss of plasticiser and also an increase in crosslinking.

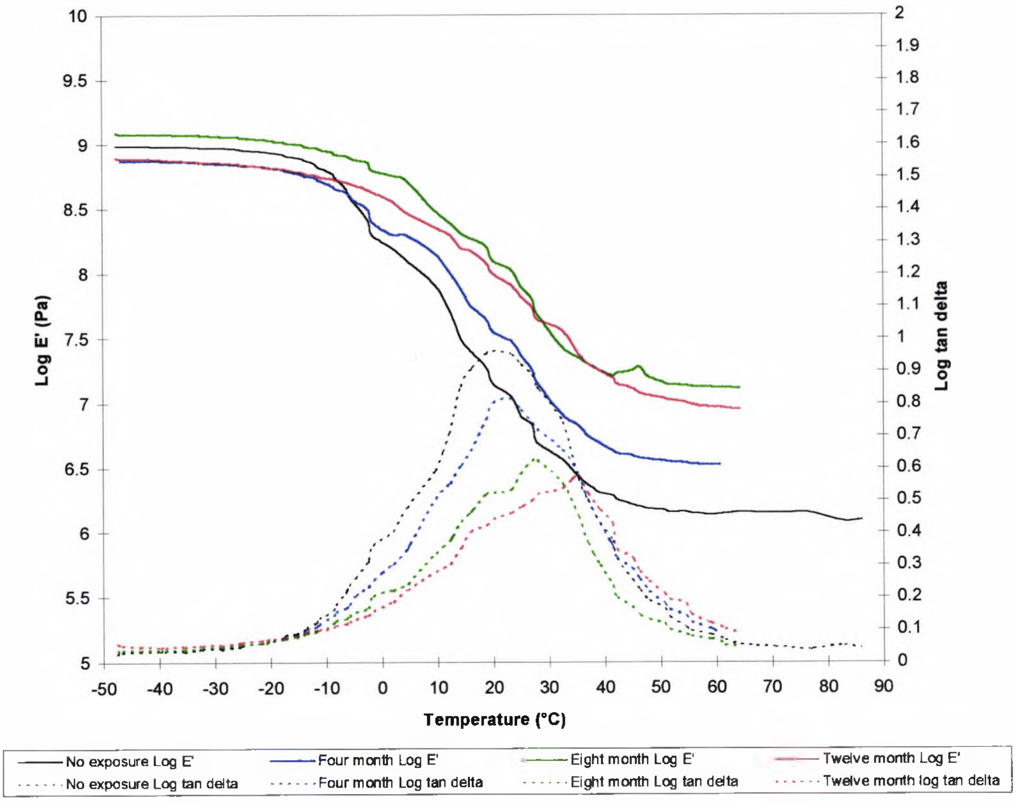


Figure 9.3.1.2.a. The effect of up to twelve months natural weathering on System 1

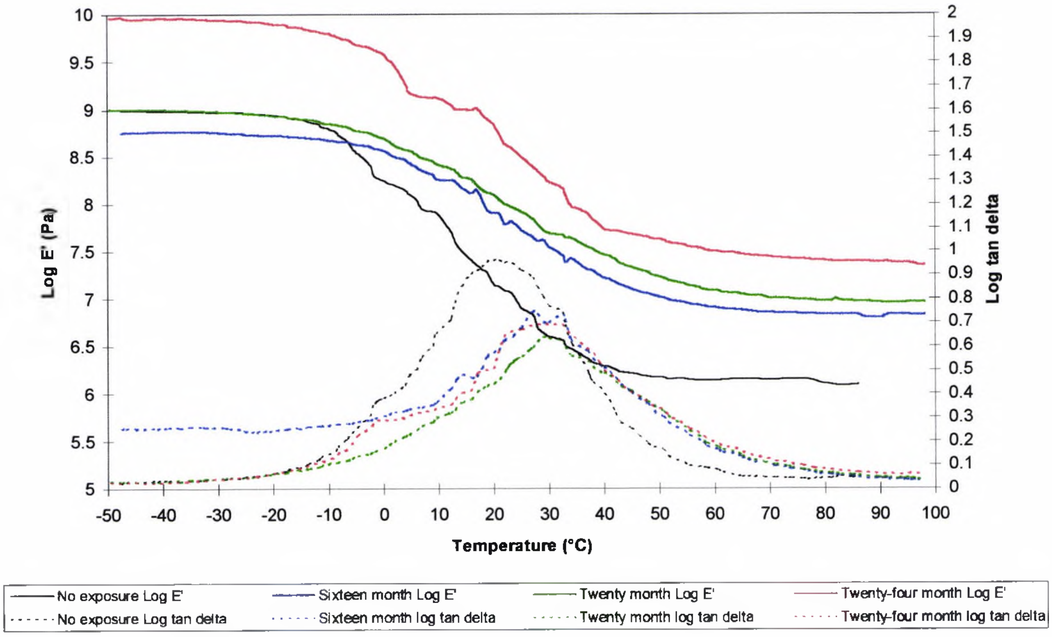


Figure 9.3.1.2.b. The effect of up to twenty-four months natural weathering on System 1

If the initial plasticisation was due to low molecular weight polymer or oligomer, and they take part in further crosslinking reactions, the two processes of crosslinking and loss of plasticisation would occur in one step. Low molecular weight polymer could be sufficiently insoluble in water and dichloromethane to be detected in the analysis for non-volatile plasticisers.

Another explanation is that volatile autoxidation products remain in the young film, and thus plasticising it. As additional crosslinking occurs, these compounds would continue to be generated, only to be lost from the film by a process akin to evaporation. These would, however, be expected to be removed by heating, but the volatile content of all the coatings remained fairly constant at 95 to 99% w/w throughout the exposure period.

The glass transition temperature of alkyds has been shown to depend on seasonal variations (Section 9.3.1.1), and similar reasoning can be used to explain the shift in the maximum value of log tan δ.

The exposure of these films began in December, so the one examined after four months was withdrawn in April. As the solar energy (and mean temperature) in early spring is less than in the summer months, loss of any volatile material would be expected to be reduced. Over this period, the maximum value of log tan δ is not shifted to a higher temperature, indicating that loss of plasticisation does not, indeed, take place. Additional crosslinking does however occur, as indicated by the drop in the maximum value of log tan δ. If oligomers or low molecular weight polymer were used in additional cross-linking reactions, they would not be the main cause of plasticisation. Since there is no significant change in volatile content, the coatings are unplasticised at this stage.

After eight months exposure (panel withdrawn in August) the coating has had opportunity, owing to both increased solar radiation and increased mean temperature, to displace any autoxidation products generated. The reactions of low molecular oligomers and/or polymers could also be initiated. As the maximum log tan δ point has shifted down and to a higher temperature, the implication is that oligomer and/or low molecular weight polymer is the cause of this change.

The T_g for System 1 continued to rise throughout the exposure period (Table 9.3.1.1 and Figure 9.3.1.1), but the value of the maximum of the log tan δ plot remains constant (within experimental error) at about 0.65 and 30 °C.

The log of the storage modulus, however, does increase over this period. As tan δ is the ratio of the loss modulus to the storage modulus, the loss modulus (not measured directly by the DMTA) must also increase at the same rate as the storage modulus. This implies that there is both an increase in chain length (causing the increase in storage modulus) and either an increase in lower molecular weight polymeric material, or an increase in the number of side chains (both factors would impede the movement of the main polymer backbone, and thus increase the energy lost). As the temperature at which the maximum log tan δ value occurs remains constant, the implication is that increased plasticisation does not occur. This deduction is supported by failure to determine any increase in volatile nor non-volatile extractable material.

9.3.1.3. System 2

System 2 is a coating based on a solvent borne modern flexible alkyd resin (the same resin used for Systems 1 and 3), formulated as a semi-transparent stain with iron oxide pigment. Examination of Figures 9.3.1.3.a and 9.3.1.3.b shows that, up to twenty months, the value of the log of the storage modulus below the glass transition temperature is approximately constant (like System 1). The slight variations probably reflect the effect of errors incurred in measuring the dimensions of the coating (which are used to calculate the value of the modulus). By twenty-four months exposure, log E' has increased dramatically.

As with System 1, the storage modulus of the rubbery state increases after natural exposure. Unlike System 1, however, there is no increase in the first four months, implying that the iron oxide is able to protect the film from change in spring sunshine. The reactions are therefore initiated by radiation, probably UV; the brown System 2 would be expected to get hotter than the clear System 1, and so, if additional crosslinking reactions were initiated by heat from the solar energy, System 2 would be expected to crosslink at a greater rate than System 1 (the slight drop in maximum value of log tan δ for the four month old film is probably within experimental error).

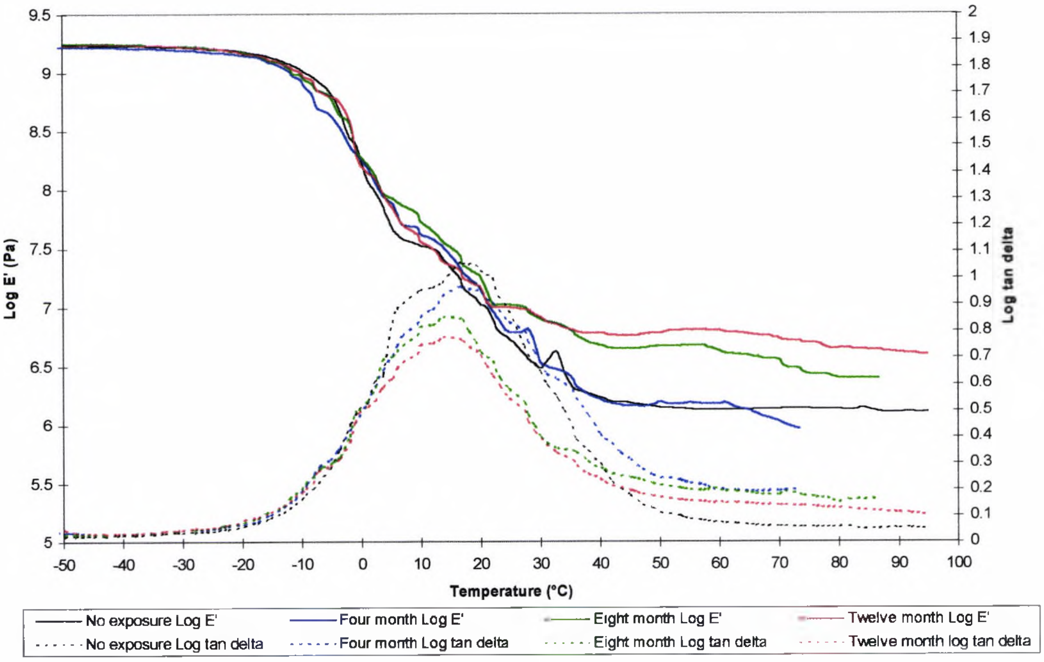


Figure 9.3.1.3.a. The effect of up to twelve months natural weathering on System 2

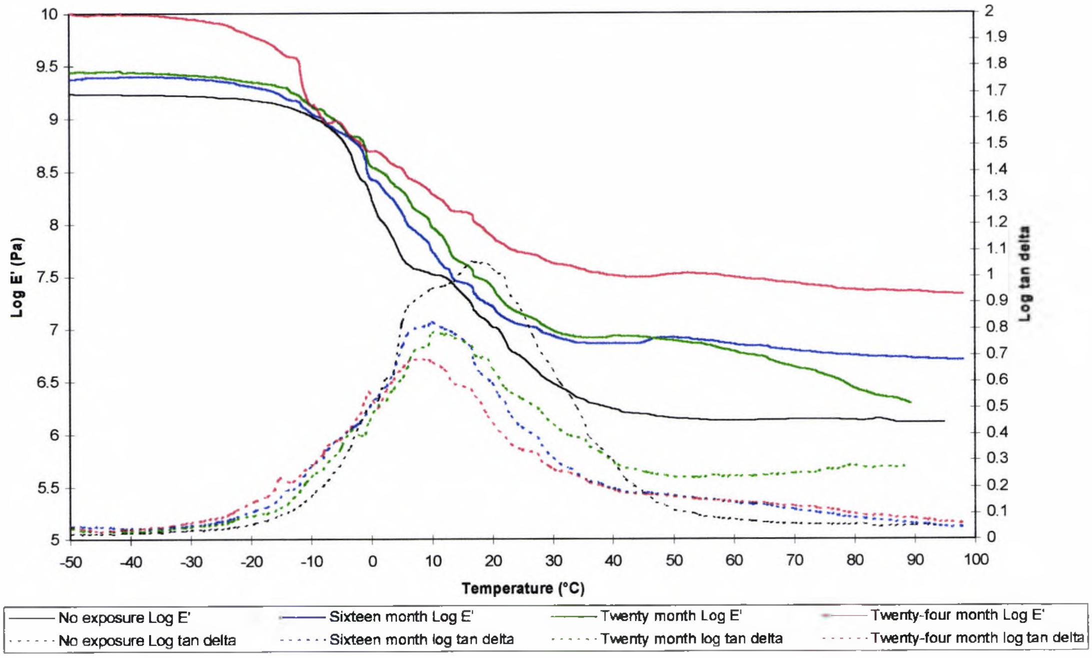


Figure 9.3.1.3.b. The effect of up to twenty-four months natural weathering on System 2

By August, after 8 months exposure, the log storage modulus above the glass transition temperature jumps from about 6.1 Pa to about 6.7 Pa. There is a corresponding drop in the maximum value of log tan δ, from about 1 to about 0.8, indicating that the increase in storage modulus is due to an increase in crosslinking density.

Although there is an apparent small increase in log storage modulus after the T_g from eight to twelve months exposure, followed by a small drop for the sixteen and twenty month old films, these variations are expected to be within experimental error. By twenty-four months exposure, the storage modulus has increased dramatically, both below and above the glass transition temperature. This is accompanied by a corresponding drop in the maximum value of log tan δ, indicating that the stiffness increase is due to crosslinking.

On increasing natural exposure, there is a reduction in the temperature at which the maximum value of log tan δ occurs, from about 19 °C for the unexposed film, to 9°C for a twenty-four month old film. This would imply that the film is being increasingly plasticised. There is no corresponding increase in either volatile or non-volatile material, which appears to contradict the last observation.

Close examination of the unexposed curve reveals that it is comprised of two, overlapping peaks, one at 19°C, and the other at 9 °C. This coating has three alkyd resins, two of which are present in Systems 1 and 3. The third alkyd only forms about nine percent of the dry coating weight (being used solely to enhance the dispersion of iron oxide pigment).

Examination of the temperatures of the maximum value of log tan δ for unexposed Systems 1 and 3 (Figure 9.2.1) indicate that the log tan δ peak at 19°C is due to the major resins, Synolac 6005W and Synolac 6006W, which are present in all three coatings (and at the same proportion to each other). Therefore the temperature shift is 5 °C between DSC and DMTA, for this resin blend and the DMTA frequency of 0.1 Hz.

Assuming that the Sicoflush Yellow alkyd will be shifted by approximately the same amount, a peak in log tan δ would occur at about 2 °C as this alkyd has a glass transition temperature (as measured by DSC) of -3 °C. This implies that the alkyd used in the pigment dispersion does not contribute to either of the two log tan δ peaks observed for System 2.

Another implication is that iron oxide can influence the crosslinking reactions, and that this influence, although significant for an unexposed film, becomes increasingly important as the film ages. The ability of iron oxide to affect autoxidation reactions, and the effect on DSC initial values has already been discussed (Section 9.2.1.1.2.). What the DMTA results show, however, is that the structure of the polymer backbone is altered within sixteen months of natural exposure when in the presence of iron oxide (Section 5.2.1.).

9.3.1.4. System 3

System 3 is a coating based on a solvent borne modern flexible alkyd resin (the same resin used for Systems 1 and 2), formulated as a white, opaque paint with titanium dioxide pigment. Examination of Figures 9.3.1.4.a and 9.3.1.4.b, showing the effect of up to twenty-four months natural exposure, shows the value of the log of the storage modulus below the glass transition temperature dropping for the four month old film.

While this drop is larger than would be hoped if it were due to experimental error, it is difficult to ascribe another explanation. Unlike Systems 1 and 2, there is no sudden jump in stiffness for the twenty-four month old film, indicating that the DMTA itself did not impart that change due to, for example, an error in calibration.

Above the glass transition temperature, the log of the storage modulus changes little over the first twenty months, but appears to rise after twenty-four months exposure. While we have seen that large errors can be generated, the difference in stiffness above and below the glass transition temperature does tend to be reduced with increasing exposure time; the unexposed film having a difference of 1.9 Pa, the twelve month old 1.5 Pa, and the twenty-four month old only 0.9 Pa.

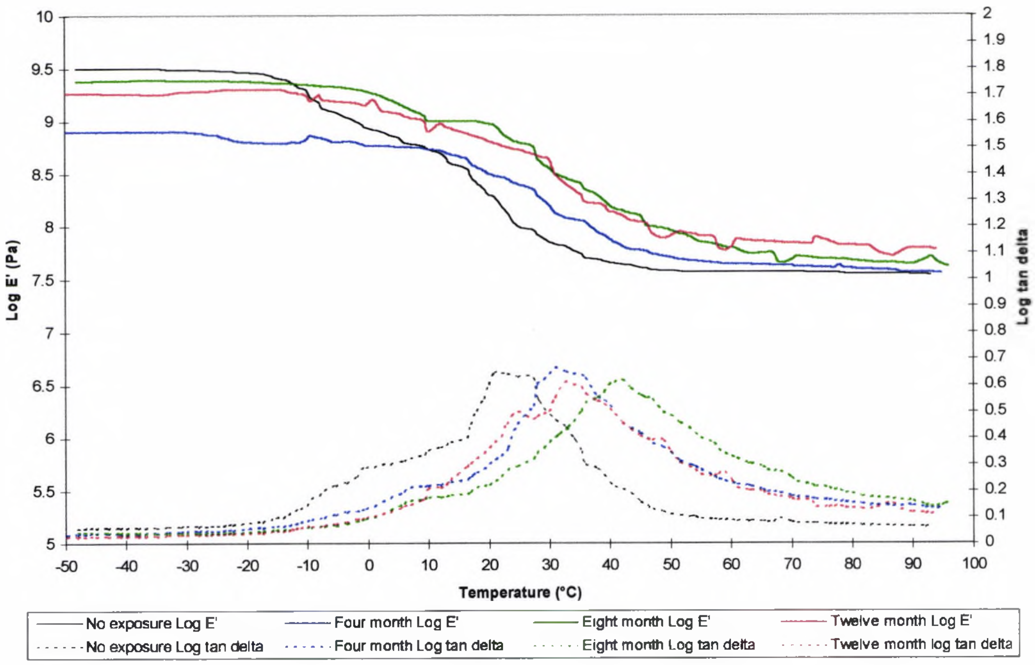


Figure 9.3.1.4.a. The effect of up to twelve months natural weathering on System 3

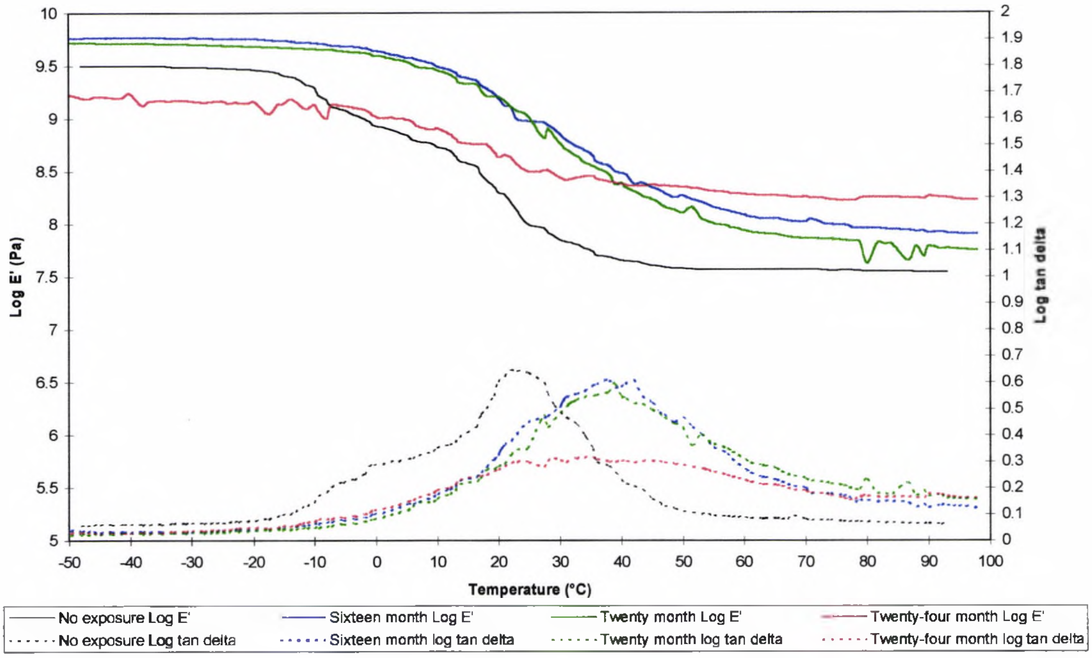


Figure 9.3.1.4.b. The effect of up to twenty-four months natural weathering on System 3

The height of the log tan δ maximum is less than for Systems 1 and 2, but this has already been attributed to increased pigmentation (Section 9.2.1.1). The interesting observation to be made, is that the height does not drop until twenty-four months. This implies that the titanium dioxide pigment is able to protect the coating from change (i.e. additional crosslinking reactions) for over twenty months. That is inconsistent with the values of T_g, but the T_g measurements were carried out on thinner films, and were exposed at a different time. By twenty-four months, however, the height has dropped dramatically, indicating a large increase in crosslink density has occurred.

The temperature at which the maximum value of log tan δ occurs does, however, vary. When the time of year is considered with the temperature of the maximum value of log tan δ, a pattern emerges. The panels were exposed in December. By April (the four month old film), the maximum has increased by 7°C, and by August it has increased to 17 °C above the unexposed temperature. In the following December (twelve months), the temperature has dropped back, almost to the four month value, but for the sixteen month and subsequent films (from the following April), the temperature has jumped to 39 °C.

This could be due to plasticisers being “baked” out of the film. This implies that crosslinking reactions could still be taking place, generating autoxidation products, but, if so, degradation would have to take place at an equal pace. Another possibility is that the first year merely removed tightly bound autoxidation products, and these were replaced in the second winter by other plasticisers (e.g. water).

Non-polar non-volatile material was two to three times higher for the unexposed, four and twenty-four month old films, than the other ages, indicating that the initial loss of plasticisation is indeed due to a "baking" process over the summer months. These are not replaced by volatile plasticisers since the non-volatile content remains constant at 97 to 99 % for the entire exposure period. This implies that competing crosslinking and degradation reactions are generating the plasticisation.

9.3.1.5. System 7

System 7 is comprised of three paints, each based on the same solvent borne alkyd resin, and formulated to represent a traditional white paint, being applied as primer, undercoat and topcoat.

Figure 9.3.1.5.a shows that the value for the log of the storage modulus below the glass transition temperature is approximately constant (within experimental error) for the first twelve months of natural exposure. Figure 9.3.1.5.b shows that this value tends to increase in the second year, but this increase is within the experimental error.

Like the flexible alkyd based coatings (Sections 9.3.1.2 to 9.3.1.4), there is an increase in the value of the log storage modulus on natural exposure. Unlike these systems, however, the increase occurs immediately, but does not then increase further (within experimental error).

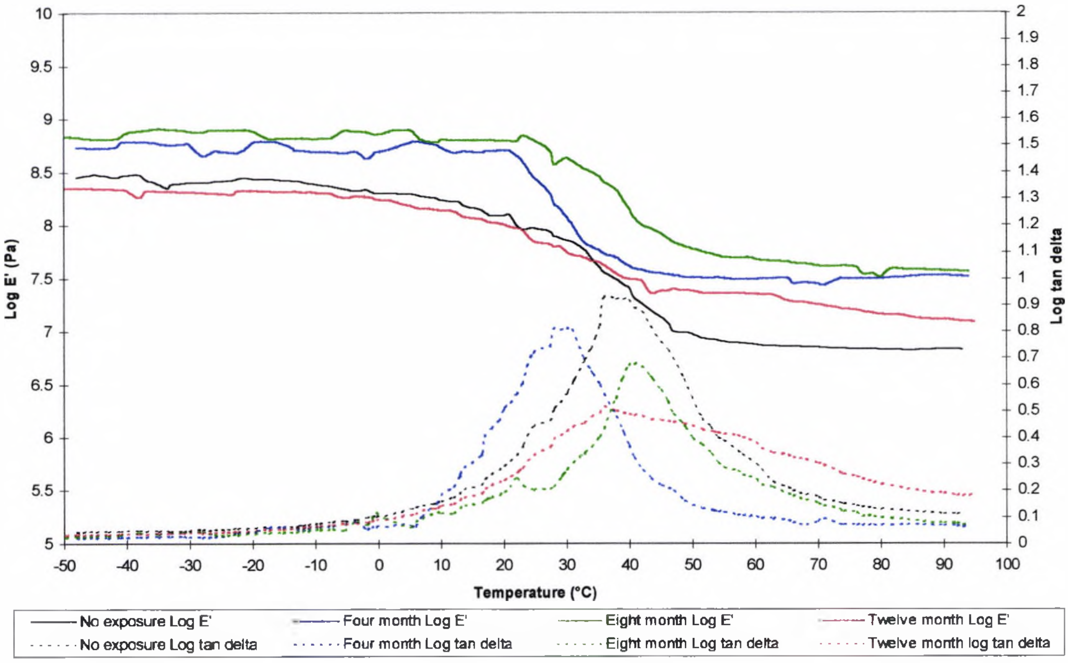


Figure 9.3.1.5.a. The effect of up to twelve months natural weathering on System 7

This observation is even more surprising when the crosslink density (i.e. the fall in value of the maximum of the log tan δ curve) is examined over this period. There is, indeed, an initial drop from the unexposed to the four month old film (accompanied by a shift to a lower temperature indicating in increase in degree of plasticisation possibly due to retained autoxidation products), but the value continues to drop for the eight and twelve month old films.

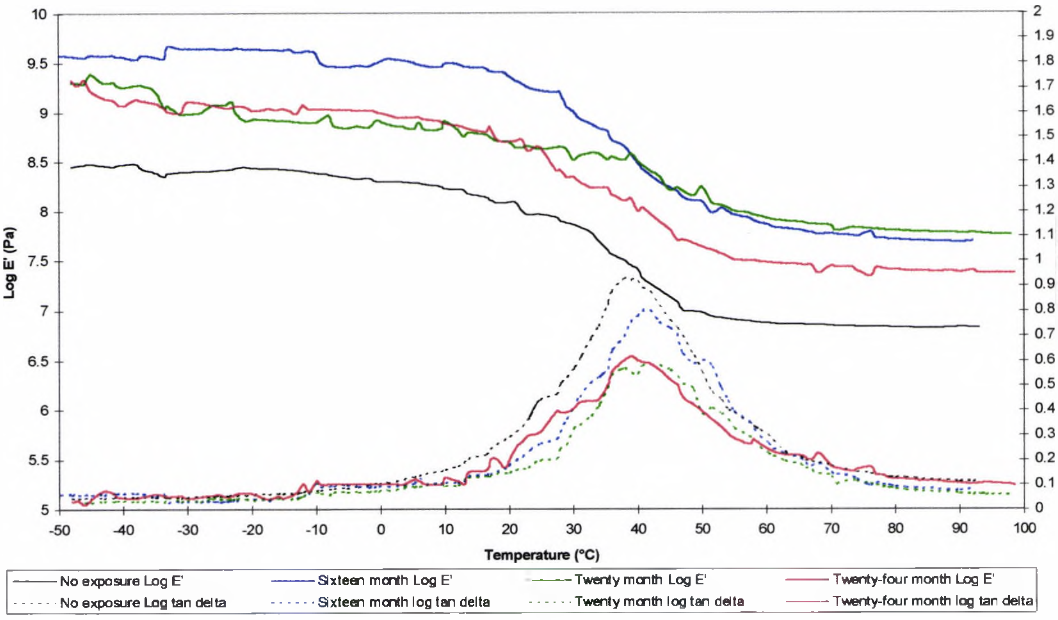


Figure 9.3.1.4.b. The effect of up to twenty-four months natural weathering on System 7

As tan δ is the ratio of loss modulus to storage modulus, this implies that, for this alkyd, the increase in crosslink density first increases the storage modulus at temperatures above the glass transition temperature, but then merely reduces the loss modulus (which is not measured directly). After one year has elapsed, this increase in crosslinking then increases the storage modulus below the glass transition temperature.

Between twelve and sixteen months natural exposure, there is an apparent decrease in crosslinking density, to the four month old value. This increase in log tan δ value is thought to be greater than that due to experimental error, and corresponds to an increase in log storage modulus. As tan δ is the ratio of loss modulus to storage modulus, the loss modulus (which was not measured directly) must be very large.

The reason for the increased value for tan δ and loss modulus is not known. It cannot be due to increased plasticisation since the temperature at which log tan δ reaches a maximum is not changed. Also analysis for plasticisers did not show significant variations over the exposure period.

Another possible explanation is that the pigmentation concentration (which affects the height of the log tan δ peak - Section 9.2.1) has been reduced from the second December (twelve months) to the second April (sixteen months). This could conceivably be caused by extensive chalking (Section 1.4.1) were it not for the fact that chalking denotes that the binder has eroded away.

A similar effect might be expected if the binder no longer “wetted” the pigment, possibly due to the photochemistry of titanium dioxide, but such photoactivity would be expected to occur during the summer months, and not in the early spring. Another drawback to this theory is that disassociation between the resin and pigment would not increase the absolute amount of resin being measured by the DMTA, and so the height of the log tan δ peak would not increase.

If this increase was due to faulty calibration of the DMTA, other systems run at a similar time would be expected to be affected, but they are not.

The height of the log tan δ peak for the twenty and twenty-four month old films is back to that of the twelve month value, further supporting the view that no overall change in degree of crosslinking occurred in the second year of natural exposure.

9.3.2. Acrylics

It will be interesting to firstly examine, fairly superficially, the acrylics in general, in terms of the effect of pigmentation and type of acrylic. Each system in turn can then be studied in more detail.

9.3.2.1. Acrylics generally

The effect of natural weathering on the two coatings based on the same acrylic resin, System 4 (with semi-transparent iron oxide) and System 5 (with iron oxide and mica as an opaque), is shown in Table 9.3.2.1 and also Figure 9.3.2.1.

Table 9.3.2.1. The effect of natural weathering on the T_g of acrylics, as determined by DSC. The uncertainty is thought to be ±1 °C.

	System 4	System 5
No exposure	5 °C	6 °C
4 months	5 °C	6 °C
8 months	8 °C	7 °C
12 months	11 °C	10 °C
16 months	9 °C	9 °C
20 months	8 °C	6 °C
24 months	11 °C	6 °C

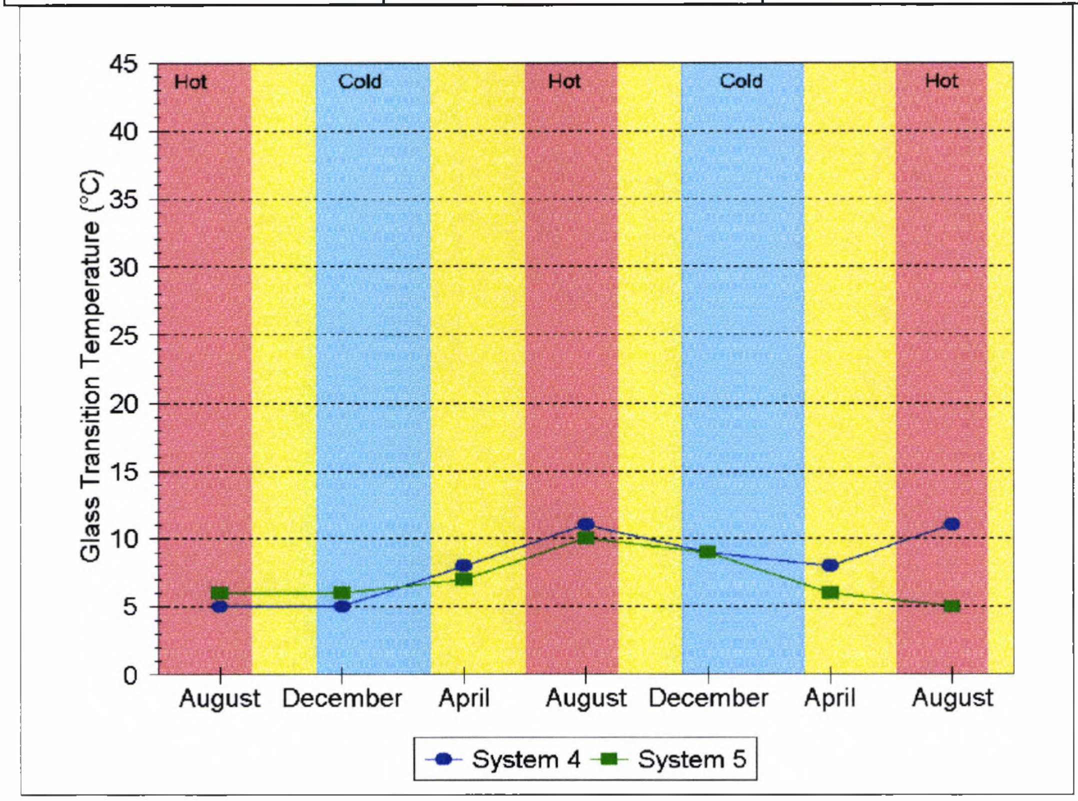


Figure 9.3.2.1. Variation of T_g of acrylics with month of measurement.

Unlike alkyds, acrylics do not embrittle immediately on exposure, reflecting the fact that they are polymerised before application. This conflicts with the findings of Perera and Oosterbroek[174] who found that the T_g increased due to increases in tensile and compressive stresses. Their work, however, studied the effect of accelerated weathering on acrylic/urethane and acrylic/melamine co-polymers.

The increase over the winter months (month 8) is almost certainly due to the leaching of low molecular weight oligomers and other plasticising agents from the coatings during the wet winter months. This implies that either there was insufficient rainfall between August and December to leach out these compounds, or that a period of frost was required to free the plasticisers (possibly by differential expansion "ripping" the plasticisers from their "bound" sites). This theory is supported by the fact that more polar and non-polar non-volatile material could be extracted from the young films than the aged films.

By August, there is enough solar energy to promote radical reaction, probably due to a donor and acceptor mechanism, and, at this stage, these tend to favour the formation of higher molecular weight polymers.

Over the late summer months, the trend appears to be toward a slightly lower molecular weight polymer, as evidenced by a slight reduction in the T_g of both System 4 and System 5.

The downward trend in T_g is continued over the winter months (twenty months). This decrease can not be due to adsorbed plasticising agents because analysis for these proved to be negative.

After two years exposure, the differences between the relatively unprotected System 4 and the well protected System 5 (System 4 only having about one thirtieth of the pigment content of System 5) become apparent. System 4 is now embrittling (although not necessarily becoming brittle at room temperature). Conversely, reactions in System 5 appear to favour a chain shortening pathway, due to degradation reactions. The differences between the two coatings can only be due to pigmentation effects (either the different concentrations of iron oxide, or the different grades of iron oxide, or due to the mica in System 5).

It would be misleading to compare crosslinking density or molecular weight between alkyds and acrylics using T_g, because the relationship between T_g and molecular weight would be expected to vary from polymer to polymer and the polymers involved are very different.

9.3.2.2. System 4

System 4 is a waterborne coating based on an acrylic resin, formulated as a varnish with iron oxide. Figure 9.3.2.2.a shows that there is little change in the coating during the first year of exposure. In the second year (Figure 9.3.2.2.b), a number of interesting things occur. There is a jump in the value of the log of the storage modulus, both above, and below, the glass transition temperature. This is accompanied by a decrease in the maximum value of log tan δ, which also shifts to a lower temperature. Another interesting finding is that the film can be heated to 100 °C without the same degree of softening that occurred for the unexposed film.

There are a number of possible reasons for this behaviour. Clearly all must explain an increase in cross linking density with increased plasticisation, leading to greater stiffness.

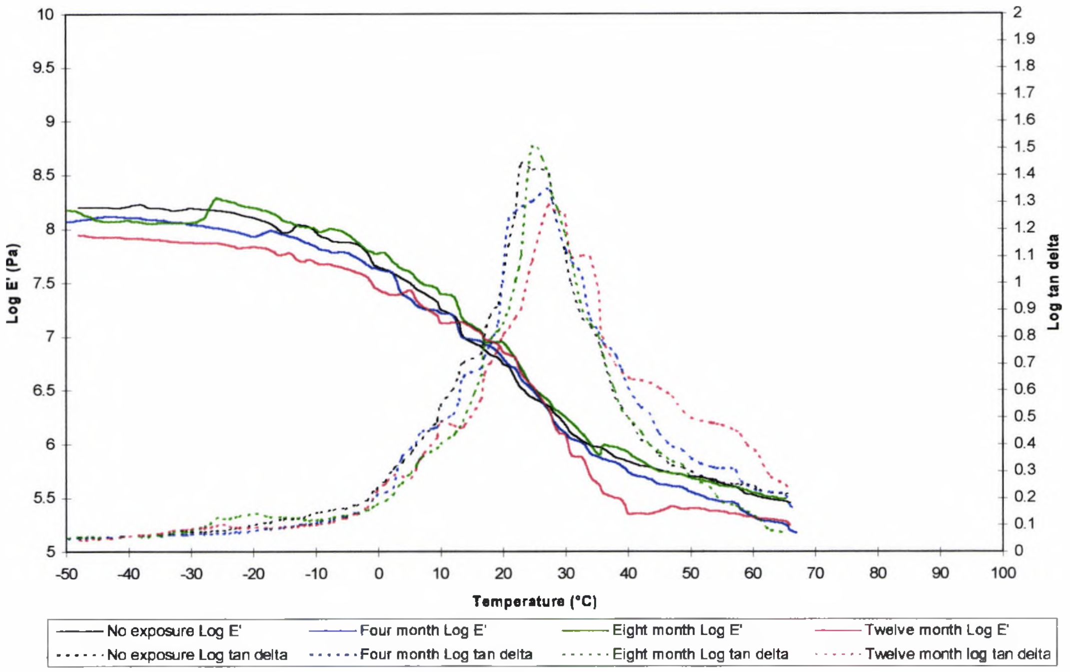


Figure 9.3.2.2.a. The effect of up to twelve months natural weathering on System 4

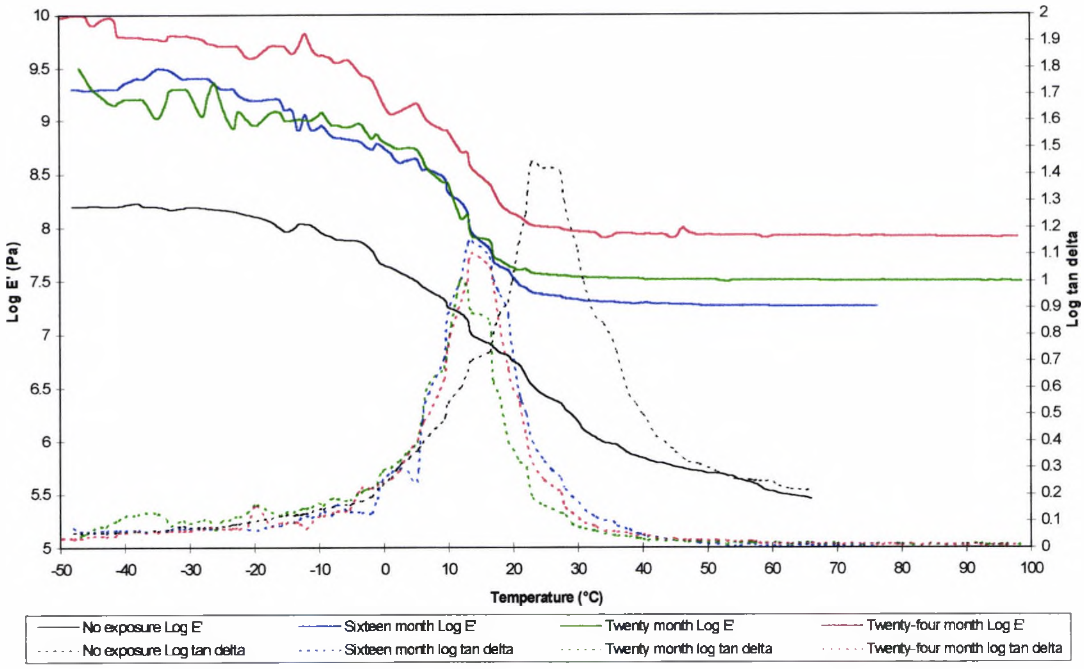


Figure 9.3.2.2.b. The effect of up to twenty-four months natural weathering on System 4

One explanation is that the climatic conditions between December and April can degrade the coating and result in an increase in the proportion of low molecular weight material. This is a period in the year when one may expect UV light (in the form of spring sunshine) and water (both as condensation and rainfall) to coincide. That combination could lead to a combined hydrolytic and photocatalytic attack, possibly by the additives in an acrylic resin acting as donors of free radicals, possibly with water being the acceptor. Such a reaction would produce radicals within the polymer matrix, causing opportunities for both degradation (creating low molecular weight polymer or oligomer, acting as plasticising agents) and embrittlement (causing an increase in crosslinking density and stiffness). Photohydrolytic reactions with iron oxide are also possible. Analysis for plasticising material proved to be negative, which indicates that no chemical reactions which generate low molecular weight material are taking place.

It is inevitable that the process of manufacture of the resin will result in a product with a range of molecular weights and this leads to a second possible explanation. In the unexposed resin the materials of various (low/high) molecular weight are intimately mixed. During the exposure this material is exposed to a regime of alternate heating and cooling in consequence of which the fractions could become segregated (by a process akin to recrystallisation). This would result in a matrix of high molecular weight material with separate regions of low molecular weight. A problem with this theory is that the polymer chains would have to be mobile enough to segregate into two phases.

A third hypothesis requires the acrylic resin to be heterogeneous after manufacture. Heterogeneity on the molecular scale is well documented[175,176], usually for dissimilar monomers which, had they not been copolymerized, would have been incompatible. O'Conner and Orler[177] found that microdomains could be formed after annealing a copolymer. More recently, Soltani et al[178] found that block copolymers of methyl methacrylate and butyl acrylate had similar domains on manufacture. If these domains contained polymer of differing molecular weight, and became separated over the winter months, lower molecular weight "pockets" could plasticise an interconnecting higher molecular weight network.

9.3.2.3. System 5

System 5 is a waterborne coating, based on the same resin as System 4, but formulated as an opaque coating with iron oxide and mica. For an unknown reason, this coating was more difficult than other systems to study by DMTA, as the films were more prone to breaking. If loading on the clamps was increased, the detached film broke as the load was applied. If loading was decreased, the film broke at the start of the run, implying failure due to buckling. Often, a film which did not break below the glass transition temperature failed during, or after the glass transition temperature. Consequently, due to time constraints, replication for this system was reduced, often to only one run.

The most probable cause of this difficulty lies in the use of mica as a pigment. System 5 is the only coating utilising mica in the formulation. Another explanation could be that the pigmentation concentration is such that it helps propagate cracks. As the concentration of pigment (as determined by ashing) for System 5 (52%) is similar to those for Systems 3 (60%) and 7 (55%), this explanation is less likely, but possible as the acrylic resin will almost certainly have a different critical pigment volume concentration (cpvc) than the solvent borne alkyd resins.

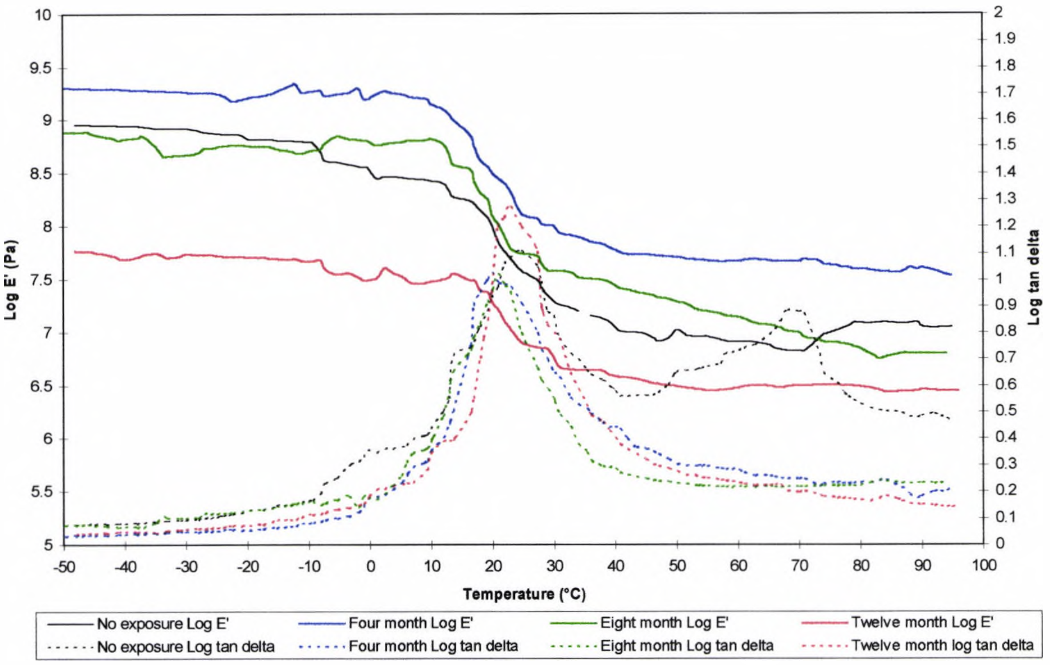


Figure 9.3.2.3.a. The effect of up to twelve months natural weathering on System 5

Figure 9.3.2.3.a shows the DMTA plots for the first twelve months of exposure. The unusual result for the unexposed film has already been explained (Section 9.2.2); the second log tan δ peak is due to the resin softening.

One may expect the double peak log tan δ plot for System 5 to continue until sixteen months since System 4 softens at about 65 °C until sixteen months exposure. By four months, however, the higher peak has disappeared, and does not return. This is accompanied by an increase in effective crosslinking, and an increase in plasticisation. While there is also an increase in the value of log storage modulus, the increase below the glass transition temperature is within experimental error. Analysis for low molecular weight material over this period proved to be negative, indicating that any plasticisation must be due to non-extractable material.

Experimental error cannot be ruled out as the cause of the increase above the glass transition temperature, due to the lack of replication. A similar increase has been observed for System 4, albeit for an older film (Section 9.3.2.2), and similar reasons can be used to explain this trend. An implication is that the increased level of pigmentation, or the presence of mica, or both, accelerates the change to the resin.

There is little change from four to eight months exposure, but a dramatic change for the twelve month old film. The twelve month old film could only be run once, for the reason detailed above. As the DMTA uses the dimensions of the film to calculate the value of the storage modulus, an error in one or more of these dimensions could, regrettably, account for the reduction in log storage modulus.

As tan δ can be expressed as the ratio of loss modulus to storage modulus, a low value for the log storage modulus would force the maximum value of log tan δ artificially high. Such an error would not affect the temperature at which the maximum value of log tan δ occurred, and so we can still say that plasticisation has been reduced between eight months exposure and twelve months exposure. There was no drop in the amount of extractable material, indicating that plasticisation is due to fairly high molecular weight material.

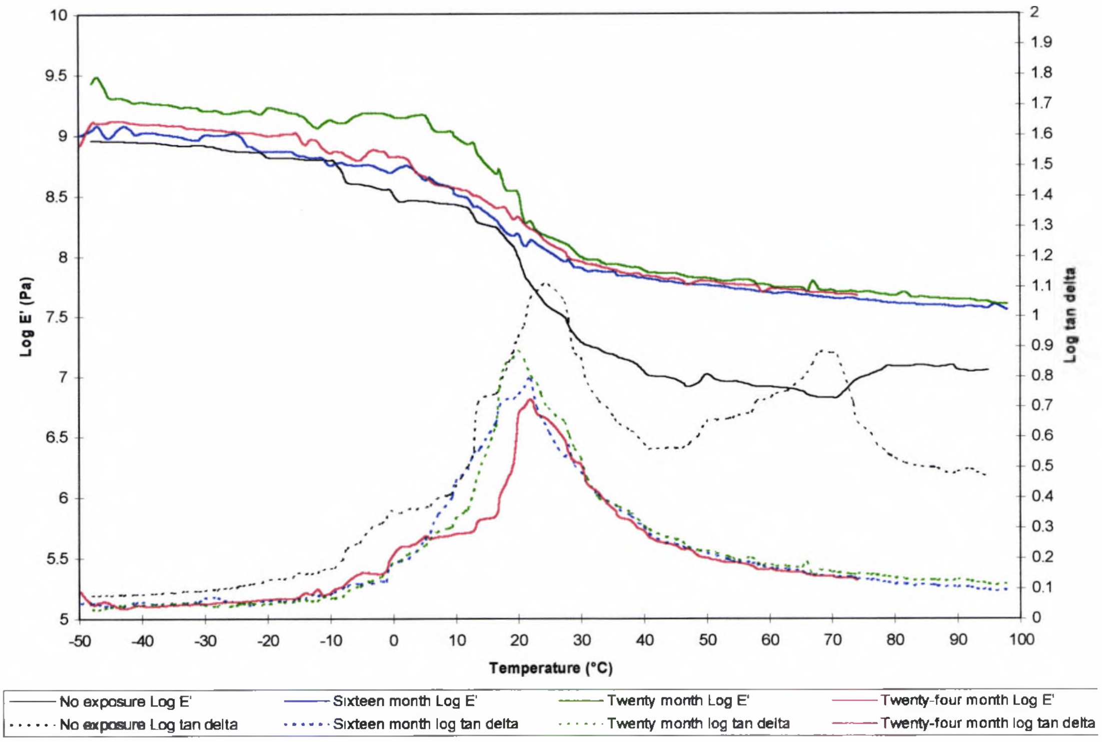


Figure 9.3.2.3.b. The effect of up to twenty-four months natural weathering on System 5

Figure 9.3.2.3.b shows the effect of between sixteen and twenty-four months natural exposure on DMTA plots, with the results for the unexposed coating also being shown for comparison. The effect of increased crosslinking, increased plasticisation and increased stiffness above the glass transition temperature (when compared with the unexposed coating) is very apparent for the second year. The reasons for this are to be expected to be exactly the same as for the four month old film, and for System 4 (Section 9.3.2.2).

9.3.3. Alkyd-acrylic Hybrid

Only one alkyd-acrylic hybrid was studied, and it was formulated as a white opaque coating using titanium dioxide, System 6 (Section 6.4). The effect of natural weathering on this coating can be seen from Table 9.3.3 and Figure 9.3.3.

The alkyd component of the hybrid allows the late summer sunshine to increase the molecular weight of the composite, and this causes an increase in T_g over the first four months.

The small increase in T_g over the late winter months (by month 8) is not due to relatively low molecular weight material being leached out since analysis for these compounds proved to be negative. Both Systems 1 and 7 (both alkyds) also exhibited an increase in T_g over this period, and so the increase could be due to additional cross-linking in the alkyd component.

Table 9.3.3. The effect of natural weathering on the T_g of an alkyd-acrylic hybrid, as determined by DSC. The uncertainty is thought to be ±1 °C.

	System 6
No exposure	7 °C
4 months	12 °C
8 months	13 °C
12 months	19 °C
16 months	18 °C
20 months	17 °C
24 months	18 °C

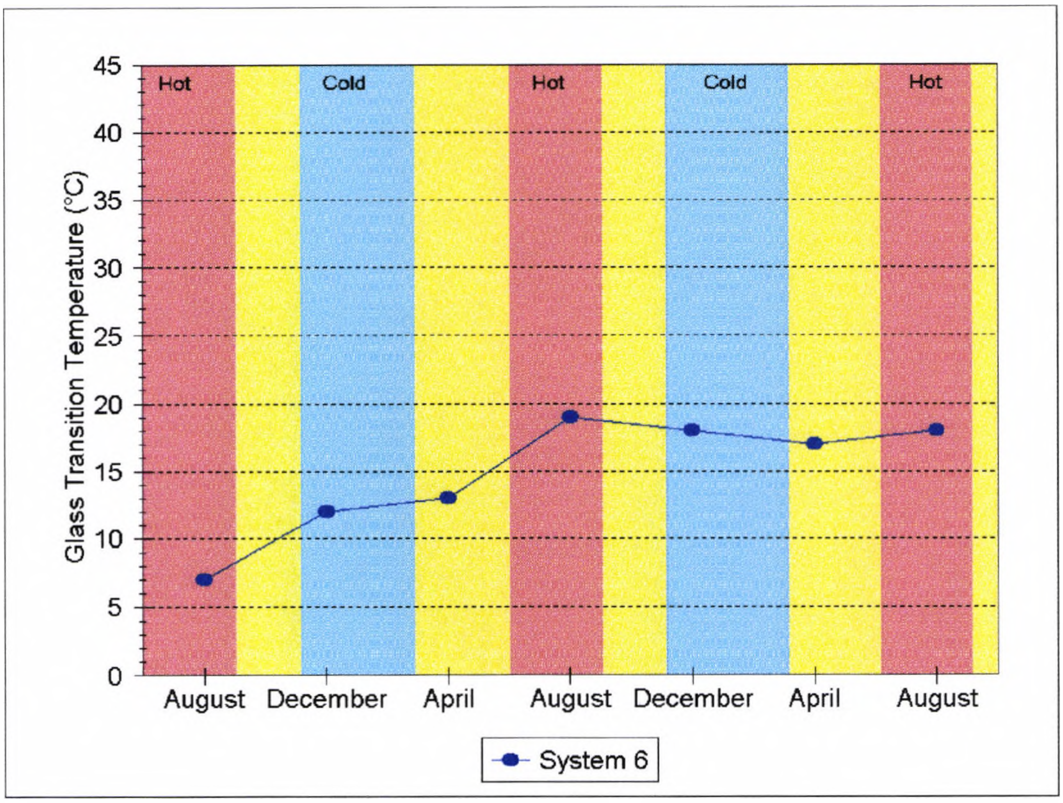


Figure 9.3.3. Variation of T_g of an alkyd-acrylic hybrid with month of measurement.

There is a sharp rise by the twelfth month exposure. Acrylic T_g tend to show a moderate rise over this period, for the reasons stated above (Section 9.3.2). The T_g of alkyds can also increase over this period. The rather dramatic increase could therefore be due to the acrylic portion, the alkyd portion, or both.

The decrease in T_g over the next four month period is more typical of the acrylic component than the alkyd component (which tend to show either an increase, or no change in the T_g). Certainly, the argument given for acrylics can equally apply to an alkyd-acrylic hybrid, namely that the photochemical reactions are tending to favour lower molecular weight polymers than in previous months.

Over the next four months (to month 20), all coatings bar System 1 show a reduction in their T_g, and System 6 is no exception. Thus the drop in T_g could be due to the alkyd portion, the acrylic portion, or both.

After two years exposure, the T_g is starting to increase again. The increase is, however, only 1°C, and so within experimental error. This is, then, not too dissimilar to the white pigmented flexible alkyd (System 3), the T_g of which remained constant.

More information about changes to the structure of System 6 can be gleaned from the DMTA data.

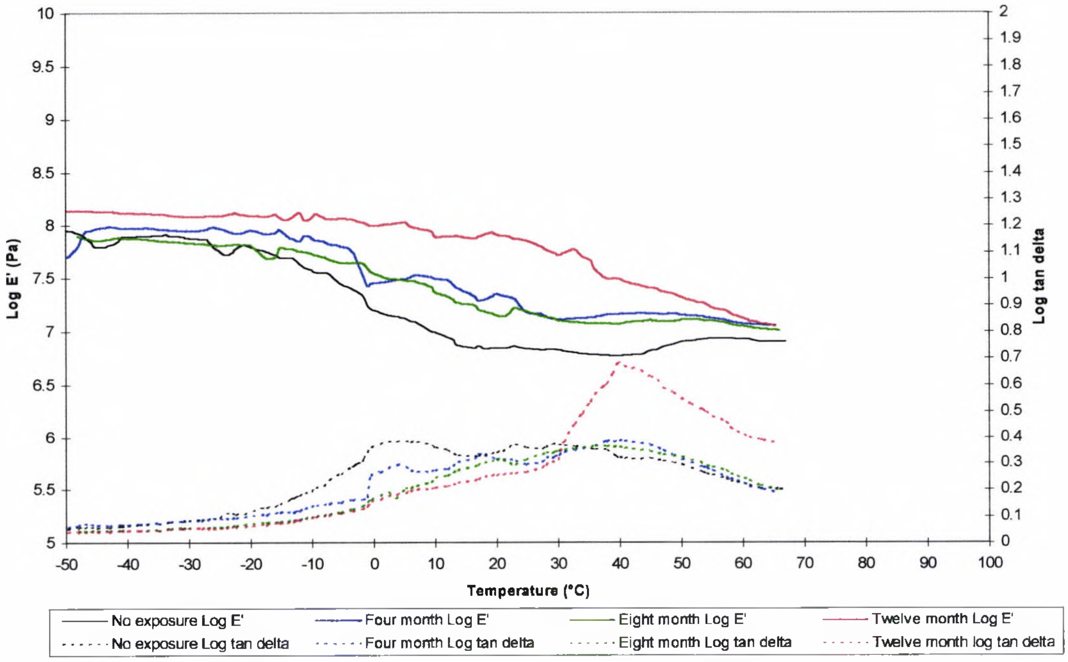


Figure 9.3.3.a. The effect of up to twelve months natural weathering on System 6

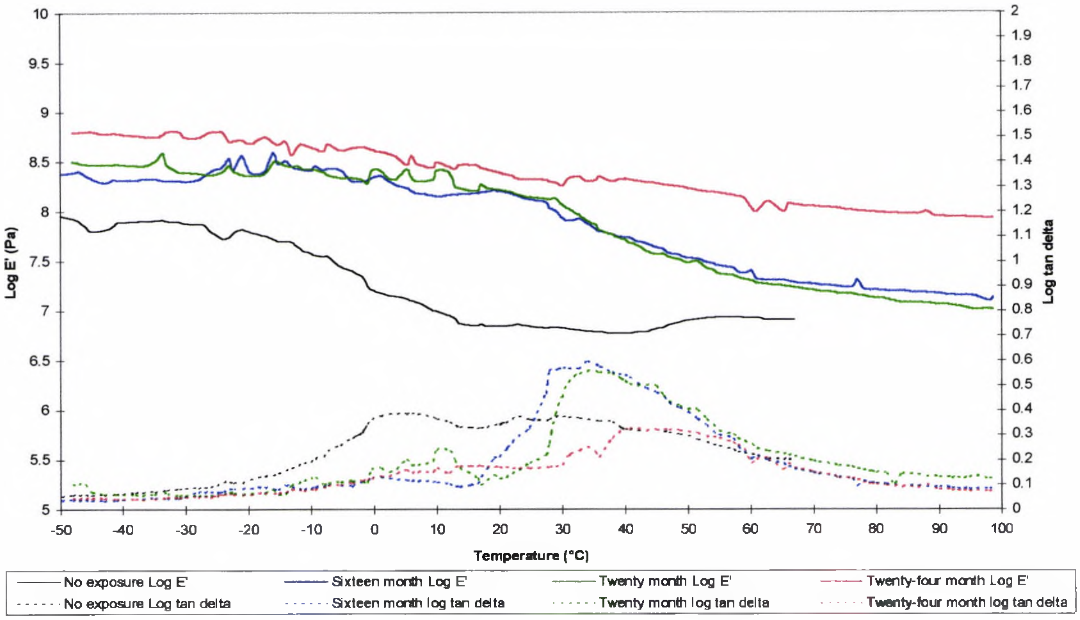


Figure 9.3.3.b. The effect of up to twenty-four months natural weathering on System 6

The two peaks in the log tan δ curve have already been attributed to the different resins (Section 9.2.3), but we can now assign the peaks to the resins by observing their behaviour during exposure. The peak occurring at the lower temperature can be seen to decrease with time, and the peak at the higher temperature stays at a constant height, then increases, then returns to its original height. With information gleaned from other systems (Sections 9.3.1 to 9.3.2), it is likely that the peak at 5 °C is due to the alkyd component, and that at the higher temperature due to the acrylic component. The alkyd peak would be expected to decrease as the alkyd cross-links until it is below the limit of detection, by eight months exposure.

One may expect three "plateaus" in the plot of the log of the storage modulus for the unexposed coating. The fact that these are not seen is perhaps due to the broadness of the acrylic peak. One explanation of the broadness of the acrylic peak is that it has a wide range of molecular weights. This could have been deliberately engineered in order to enhance the compatibility with a wide range of water borne alkyds, or to remain compatible with the alkyd whilst it changes from the low molecular weight, uncrosslinked (i.e. the “in-can”) stage to the high molecular weight, crosslinked (i.e. dried) stage.

Up to eight months exposure, the only change within experimental error, is the reduction of the alkyd log tan δ peak, indicating additional crosslinking, typical of alkyds. By eight months, this peak is undetectable. Despite this, the “cliff-top” T_g (Section 8.3 and Figure 8.3.3) is not shifted to a higher temperature until twelve months exposure.

In the plot of log tan δ for the twelve month old film, the acrylic peak has become much sharper and higher, although remaining at a similar temperature (the exact temperature shift, if any, cannot be determined due to the broadness of the peak before twelve months).

This is not accompanied by a loss in stiffness below the glass transition temperature, and, although the log of the storage modulus had not stabilised before the run was stopped, it appears to have returned to a similar value as for the unexposed, four and eight month old films. The implication here is that the acrylic component has, between August (eight months) and December (twelve months), become less crosslinked, but with a narrower range of molecular weights.

Acrylics have already been shown to have the ability to change their molecular weights in winter/spring months (Sections 9.3.2.2 and 9.3.2.3). The effect of decreased crosslinking in the acrylic component is however, real, since the maximum value of log tan δ remains constant from twelve to twenty months.

This coating is the only system which combines acrylic resin with titanium dioxide pigment. The decrease in crosslinking for the acrylic component could be due to the photochemical activity of titanium dioxide. The plots of the log of the storage modulus are also very similar. for the twelve, sixteen, and twenty month old films.

There is, yet again, a dramatic change in the autumn/early winter months, this time for the twenty-four month old film. The stiffness of the twenty-four month old film does not go through a well defined transition, the crosslink density of the acrylic component had increased (that of the alkyd component remains undetectable), and plasticisation is lost. There was a small decrease in the non-polar non-volatile extractable material (from 8% to 4%) from a twenty to twenty-four month old film.

One possible explanation for the decrease in cross linking density for the twelve month old film, and then an increase for the twenty-four month old film, is the theory of separation of differing molecular weight material on the macromolecular scale (detailed in Section 9.3.2), coupled by the protective quality of titanium dioxide,.

If differing molecular weight material did separate when cycled at certain temperatures, the higher molecular weight material could form nodules in a sea of lower molecular weight material (instead of low molecular pockets in a crosslinked matrix suggested for Systems 4 and 5 - Sections 9.3.2.2. and 9.3.2.3.). These differences are not impossible, as a different acrylic resin was used for System 6 (one intended to be used in conjunction with a water borne alkyd as opposed to one intended to be used alone).

Titanium dioxide is thought to be responsible for protecting a resin for the first twenty months of exposure (c.f. System 3 - Section 9.3.1.4). It is not inconceivable that any low molecular weight material present in the film after this time could be embrittled by radical chain termination reactions.

9.4. Fourier Transform Infra-red Photoaccoustic Spectroscopy

9.4.1 Reproducibility

Before considering in detail the results from the various systems it is necessary to ascertain the variations which may be found between samples which are nominally identical. This will lead to an understanding of the significance of apparent differences.

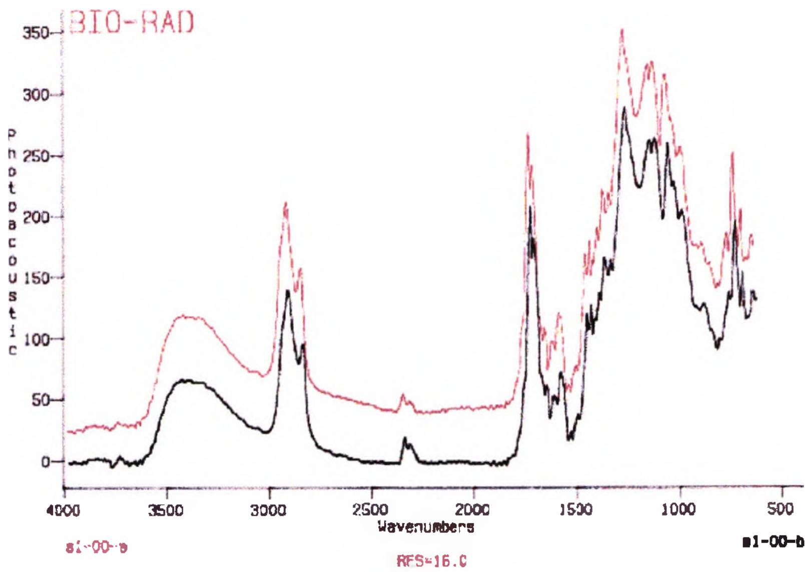


Figure 9.4.1.1. Unexposed System 1. The two spectra are taken from different samples, within a few minutes of each other.

Figures 9.4.1.1 and 9.4.1.2 show the spectra of the two discrete samples of each unexposed coating, and so represent the errors incurred from sample to sample. The differences between the two replicates is thought to arise from variations between the wooden blocks (Section 8.4.2.1).

The main difference seen in Figure 9.4.1.1 is a shift in baseline indicating a small difference in height of the two samples. Close examination of the C=O stretch between 1725 to 1650 cm^{-1} reveals that the red spectrum drawn in is shifted 10-20 wavenumbers higher than the black spectrum.

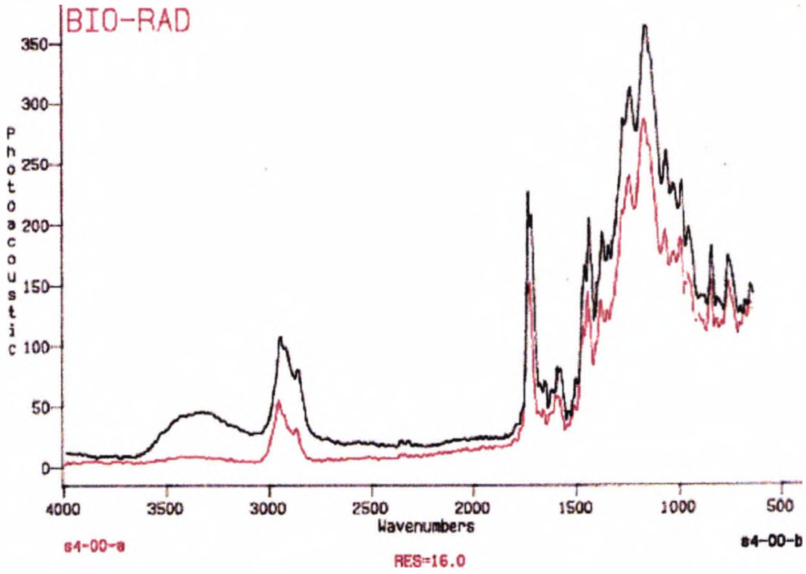


Figure 9.4.1.2. Unexposed System 4. The two spectra are taken from different samples, within a few minutes of each other.

Figure 9.4.1.2 shows that the baseline is fairly close, indicating that the wooden blocks were nearly identical in height. There are, however, a number of differences between the two spectra of two discrete samples of the same coating:

- the red spectrum is less intense than the black spectrum
- the red spectrum lacks a hydroxyl stretch between 3100 and 3600 wavenumbers
- the red spectrum is shifted 10-20 wavenumbers higher than the black spectrum between 1000 and 1800 wavenumbers

The differences between the two spectra in each case mean that quantification of changes in functional groups as a result of natural exposure will be difficult.

Another consequence is that subtracting unexposed spectra from exposed spectra would result in misleading information.

9.4.2. Alkyds

9.4.2.1. System 1

System 1 is an unpigmented coating based on a solvent-borne semi-flexible alkyd resin. Examination of Figure 9.4.2.1 shows that the chemical nature of the surface of this coating changes little with natural exposure.

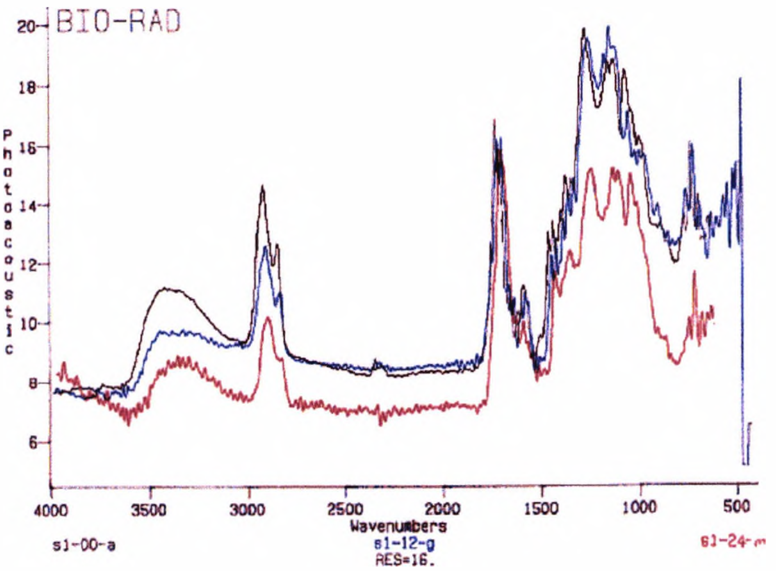


Figure 9.4.2.1. The effect of natural exposure on the infra-red spectra of System 1. The black, blue and red spectra are of the coating unexposed, and after 12, and 24 months respectively.

Close examination of the C-H stretch absorption at 2900 cm^{-1} and the C=O stretch at 1725 to 1650 cm^{-1} suggests that these absorptions are being shifted to a lower wavenumber on increasing natural exposure. This apparent shift, however, is no greater than that seen between the two unexposed coatings (Figure 9.4.1).

9.4.2.2. System 2

System 2 is based on a semi flexible alkyd resin (the same as for System 1), pigmented with iron oxide as a semi-transparent coating. Figure 9.4.2.2.a shows that, like System 1, the chemical composition of the surface changes little on natural exposure. However, unlike System 1, the shift in wavenumber for the C-H and C=O stretches appears to be more distinct. As the total shift is of the same order of magnitude as that seen for the two unexposed System 1 samples (Figure 9.4.1), this shift may again be regarded as insignificant.

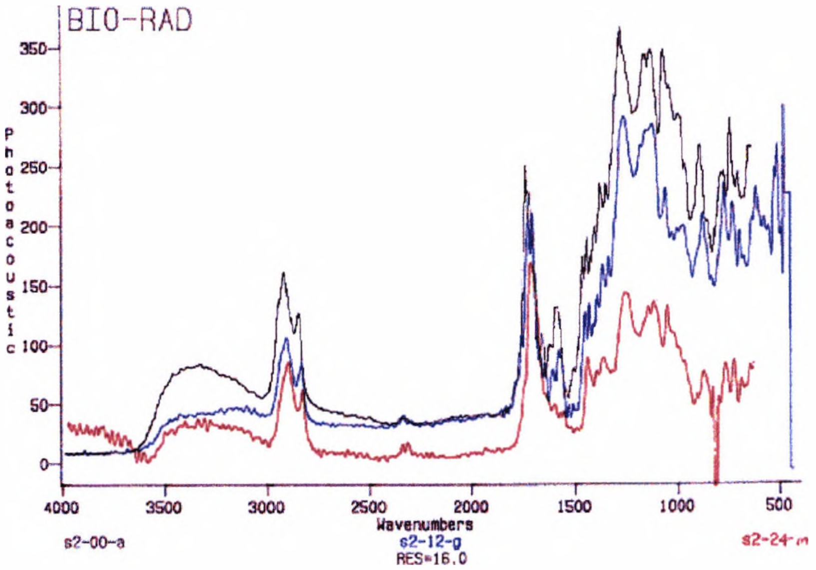


Figure 9.4.2.2.a. The effect of natural exposure on the infra-red spectra of System 2. The black, blue and red spectra are of the coating unexposed, and after 12, and 24 months respectively.

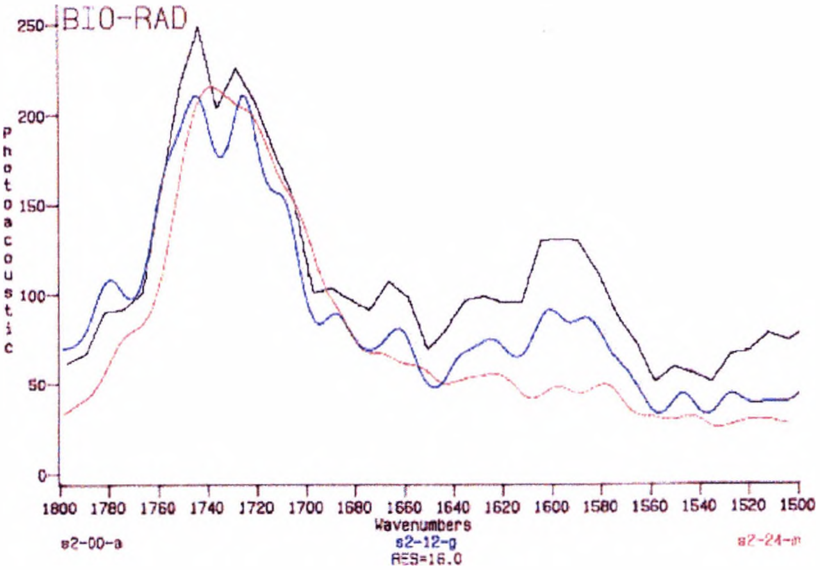


Figure 9.4.2.2.b. An expanded view of the mid range infra-red spectra of System 2. The black, blue and red spectra are of the coating unexposed, and after 12, and 24 months respectively.

A more significant variation is the behaviour of the peak at 1600 cm^{-1} (Figure 9.4.2.2.b), which could be due to a C=N stretch, a C=C stretch or a NH bend. This is present in all spectra until the spectrum for twenty-four months exposure. As the relative proportion of this peak when compared with the C=O stretch, is very different for even two unexposed blocks, it is possibly due to a contaminant. When the unexposed and 12 month spectra were re-run, the peak was no longer there, further suggesting a contaminant. If it were due to a contaminant, however, it would be expected to appear in spectra for the other coatings.

9.4.2.3. System 3

System 3 is a coating based on a solvent borne semi-flexible resin (the same as Systems 1 and 2), pigmented with titanium dioxide and calcium magnesium carbonate as a white, opaque, coating. As with Systems 1 and 2, there is little chemical change in the surface on natural exposure. The suppression of the signal for the twenty-four month old sample could be due to the onset of chalking, or due to a different gap between sample and cell window (Section 8.4.2.).

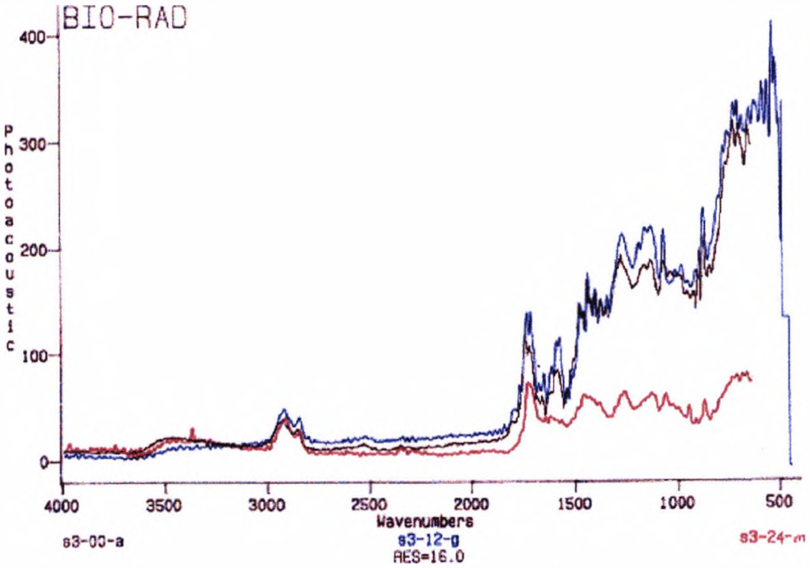


Figure 9.4.2.3. The effect of natural exposure on the infra-red spectra of System 3. The black, blue and red spectra are of the coating unexposed, and after 12, and 24 months respectively. Peaks due to the organic portion have been suppressed by the relatively high pigment content.

9.4.2.4. System 7

System 7 is a solvent borne coating based on different alkyd resin and pigments to Systems 1, 2 and 3. It is intended to represent a traditional white paint, and so is a composite of primer, undercoat and topcoat.

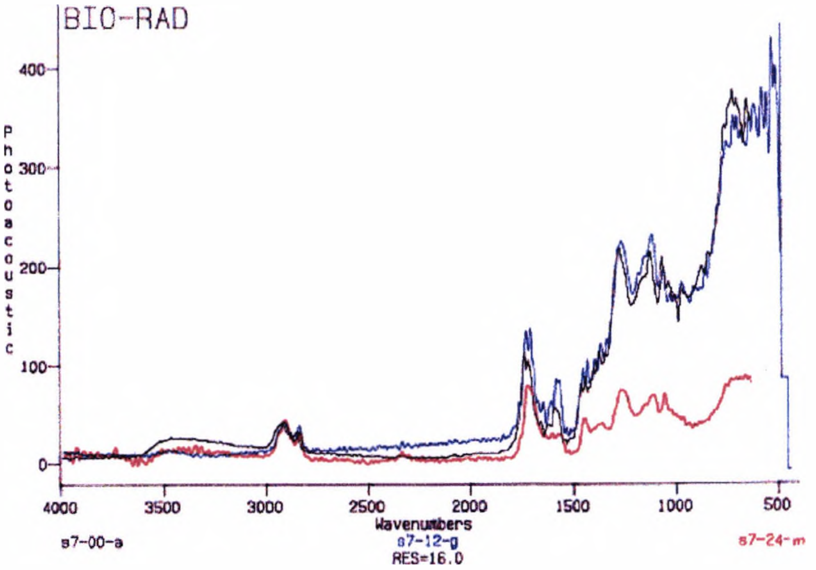


Figure 9.4.2.4. The effect of natural exposure on the infra-red spectra of System 7. The black, blue and red spectra are of the coating unexposed, and after 12, and 24 months respectively. Peaks due to the organic portion have been suppressed by the relatively high pigment content.

As with the other systems, there is little chemical change with exposure time. The peak at 1600 cm^{-1} is thought to be due to an impurity (Section 9.4.2.2). As with System 3, the reduction in signal for the twenty-four month film could be due to chalking, or due to a different gap between sample and cell window (Section 8.4.2.).

9.4.3. Acrylics

9.4.3.1. System 4

System 4 is a coating based on a water borne acrylic resin, formulated with iron oxide as a semi-transparent coating. Figure 9.4.3.1 shows that any changes in the infra-red spectrum of this system with time is within experimental error.

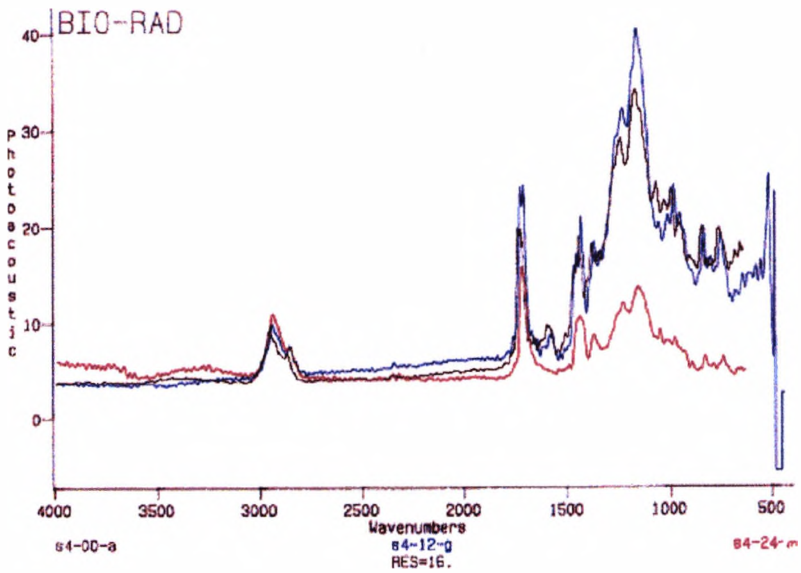


Figure 9.4.3.1. The effect of natural exposure on the infra-red spectra of System 4. The black, blue and red spectra are of the coating unexposed, and after 12, and 24 months respectively.

The spectrum of the twenty-four month old sample is suppressed, especially at lower wavenumbers, but then the relative proportion of hydroxyl (at 3500 cm^{-1}) to aliphatic CH stretch (at 2950 cm^{-1}) functional groups changes as much between two unexposed samples (Figure 9.4.1.2).

9.4.3.2. System 5

System 5 is a coating based on the same water borne acrylic resin as System 4, but formulated with iron oxide and mica as an opaque coating. Figure 9.4.3.2 shows that, for this system, hydroxyl groups (as evidenced by the peak at 3400 cm^{-1} due to the O-H stretch) decrease on natural exposure. Some caution should be applied to this conclusion owing to the large variation in this peak height observed for unexposed samples of System 4 (Figure 9.4.1.2).

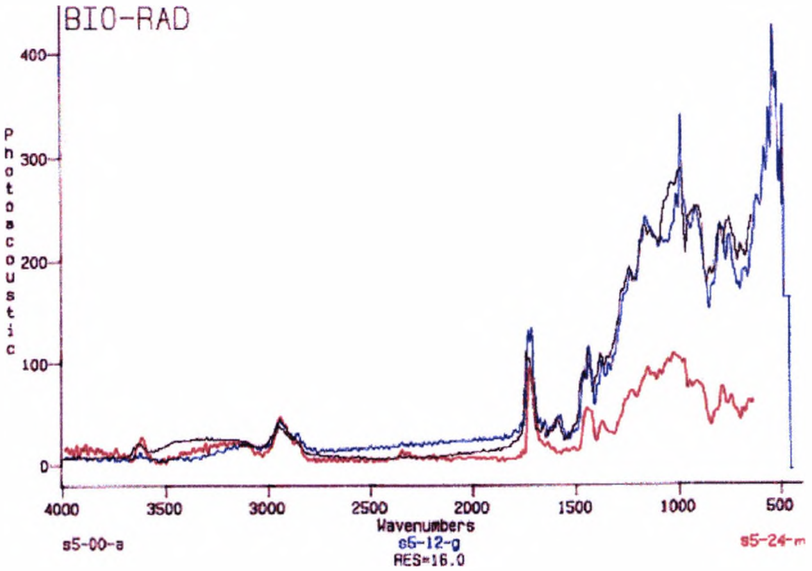


Figure 2.4.3.2. The effect of natural exposure on the infra-red spectra of System 5. The black, blue and red spectra are of the coating unexposed, and after 12, and 24 months respectively.

The band at 1600 cm^{-1} is thought to be due to an impurity (Section 9.3.2.2.), and the suppression of the spectrum of the twenty-four month old film could be due to the onset of chalking (Section 2.4.1. Figure 2.4.1.1), or due to a different gap between sample and cell window (Section 8.4.2.).

9.4.4. Hybrid - System 6

System 6 is a water borne coating based on an alkyd-acrylic hybrid. It is formulated with titanium dioxide as an opaque, white, coating.

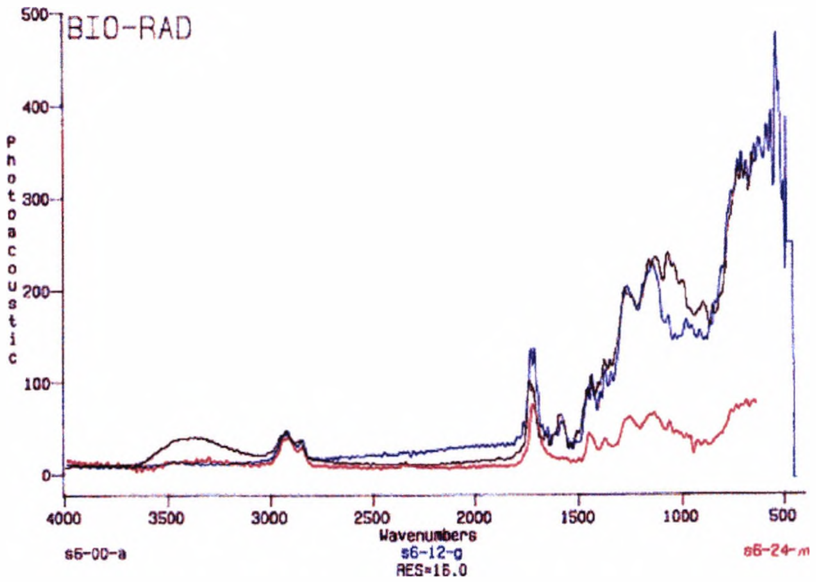


Figure 9.4.4. The effect of natural exposure on the infra-red spectra of System 6. The black, blue and red spectra are of the coating unexposed, and after 12, and 24 months respectively.

Figure 9.3.4 shows that the bands in the infra-red spectrum of System 6 due to the organic content are swamped by those due to the titanium dioxide (from 900 to 450 cm^{-1}). There is apparently a reduction in hydroxyl groups (as evidenced by the peak at 3400 cm^{-1} due to the O-H stretch) on natural exposure, but there can be similar changes in this peak height when different blocks are examined (Section 9.3.1., Figure 9.3.1.2).

The peak at 1600 cm^{-1}, although at times forming one of the strongest peaks due to the organic portion, is thought to be due to a contamination (Section 9.3.2.2.).

The suppression of peaks for wavenumbers below 1000 cm^{-1} could be due to slight differences in geometry between the blocks.

9.4.5 Summary of FTIR results

None of the coatings studied produced changes greater than those experienced from sample to sample. This conflicts directly with findings from other authors[114, 124], who found that aliphatic hydrocarbon groups were lost, and C=O groups were formed for alkyd based paints. Lemaire et al[123] found that polyvinyl chloride also gained carbonyl groups.

The reasons for this apparent discrepancy lies in the fact that the other authors did not use wood as a substrate (Hodson and Lander[114] used polished aluminium and Rasti and Scott[124] cast their alkyd resin onto a sodium chloride disk).

In hindsight, wood is expected to make a poor substrate for this technique, as the surface would not be expected to remain flat to within 3 microns (the depth of penetration by the FTIR-PAS technique) due to differential expansion of springwood and summerwood.

Another reason for the lack of repeatability is that wood grain variations prevented the wooden blocks from having exactly the same dimensions. The degree of flatness would also vary from block to block.

A third reason why poor repeatability was experienced is that the coatings were brush applied. Some variation in film thickness over the wood is to be expected with even the most skilled of painters, and this variation could exceed the 3 micron depth of penetration for this technique. Indeed System 6, the alkyd/acrylic hybrid had quite pronounced brushmarks (Figure 8.4.3).

9.5. Summary of results

Pigments have been shown to affect the T_g of resins. While this effect was only detected between iron oxide and an alkyd resin, the effect is possible between any resin/pigment combination. The effect is thought to arise from a chemical reaction, although a physical interaction (possibly caused by the difference in expansion rates as the composite goes through the T_g) cannot be ruled out.

On exposure, alkyds experience an immediate increase in their T_g attributed to solar radiation promoting free radical embrittlement reactions. Unprotected alkyds continue to embrittle, but even relatively modest levels of pigment are able to reduce that effect. It is thought that the presence of pigment promotes free radical chain scission reactions which compete with embrittlement reactions. The rate of both these reactions is determined by the seasons, presumably due to differing solar activity.

Unlike alkyds, acrylics do not immediately embrittle, due to the fact that they are crosslinked before application. Acrylics experience an increase in T_g after the winter months, and this was attributed to loss of plasticising agents. Again, there are competing chain scission and embrittlement reactions, possibly due to donor chromophores (from additives such as the thickeners), and these are influenced by seasonal variations.

After the first year, acrylics are more highly crosslinked but increasingly plasticised. There are two possible explanations (which are not mutually exclusive) for this; one being that the polymer is being segregated into high/low molecular weight domains, and the other that competing chain scission and embrittlement reactions are taking place. Certainly, the acrylic resin used "melted" at 70 °C until one year of natural exposure after which it remained "solid" up to 100 °C.

The alkyd-acrylic hybrid coating studied appeared to exhibit trends common to both "pure" alkyds and acrylics. Essentially, the alkyd component continued to cross-link, and the acrylic component ceased to "melt" after sixteen months exposure. If the hypothesis that the acrylic component segregates into different phases is true, the hybrid studied separates into a mainly low molecular weight matrix, as opposed to the "pure" acrylics which segregated into a high molecular weight matrix, plasticised by low molecular weight portions.

In general terms, the height of the maximum point of the log tan δ curve can be used to gauge the relative degree of cross-linking; the more cross-links, the lower the maximum. The height is also affected by the degree of pigmentation;

the more pigmentation, the lower the maximum. Increasing pigmentation can also increase the stiffness of the coating, especially above the T_g.

The temperature at which the maximum of the log tan δ plot occurs can be used to gauge the degree of plasticisation. If the coating becomes more plasticised, the temperature of the maximum will be lowered.

Such comparisons are only valid if the coatings have the same resin. Even the two alkyds used for System 3 (the modern opaque) and System 7 (the traditional opaque), are sufficiently different to render such a comparison invalid.

All of the coatings studied tended to increase in stiffness with increasing exposure time. This increase was more apparent above the T_g than below it.

10. Overall Summary

There are three resin types studied here, solvent borne alkyds (System 1, 2, 3, and 7), water borne acrylics (Systems 4 and 5), and a water borne alkyd-acrylic hybrid (System 6). As the photodegradation of each class is expected to be different, the results obtained for each type will be discussed in turn

10.1. Alkyds

Alkyds react with atmospheric oxygen, and form a three dimensional structure. Iron oxide (used to pigment System 2) can affect this structure as it is forming, resulting in two polymeric structures, one being the same as for the unpigmented alkyd (System 1), and the other with a lower T_g.

The evidence for these two structures lies in the DMTA results, and in particular the plot of log tan δ with temperature for the unexposed System 2 (Figure 9.2.1). This has two maxima, one at 19 °C and the other at 9 °C. A maximum at 19 °C is also seen in the unpigmented (System 1) and pigmented white (System 3) variants (Figure 9.2.1), and so was assumed to be due to the alkyd undergoing the "normal" autoxidation reactions.

The peak at 9°C was not seen in the results from the alkyd resins without iron oxide, and so had to be due to an interaction between iron oxide and the alkyd resin. The interaction is not expected to be entirely due to a chemical process, but partially due to physical processes, for example stresses caused by resin and pigment in close contact having different expansion rates.

With different chemical reactions taking place with and without iron oxide present, a difference in the IR spectra (Figures 9.4.2.1 and 9.4.2.2) might be expected. Within the limitations already discussed (Section 9.4.5) about using FTIR-PAS to study painted wood, similar functional groups were observed in similar proportions, indicating that the structure proposed by Falla[53] (discussed in Section 4.1.1.4) remains true for alkyds both with and without iron oxide.

While iron oxide has a net beneficial effect on natural weathering, it continues to modify the structure, from that of the unpigmented alkyd to the one with the lower T_g. This process can be seen in Figures 9.3.1.3.a and 9.3.1.3.b, by the shift in the maximum value of the log tan δ plot from 19 °C to 9 °C after sixteen months exposure.

The log tan δ plot can also be used to determine the degree of cross-linking - if the height of the log tan δ maximum decreases, the cross-link density has increased. As all alkyds were found to increase their cross-link density (which causes the T_g to rise) with increasing natural exposure, the net result in forming the lower T_g structure is that the T_g of the composite (as measured by DSC) remains fairly constant. No evidence of the change from one structure to the other during natural exposure could be seen in the results from FTIR-PAS (Figure 9.4.2.2).

All of the alkyds studied showed an increase in cross-link density on initial exposure. This effect was seen both in an immediate rise in T_g (Section 9.3.1), and a decrease in the height of the log tan δ peak (Figures 9.3.1.1 to 9.3.1.4). This was attributed to solar activity promoting the formation of free radicals resulting in "embrittlement". Changes in the infra-red spectra of the coatings over this period were not seen for the reasons discussed in Section 9.4.5.

The degree of pigmentation was found to have a pronounced effect on the ability of a coating to resist photodegradation. While this result was not considered surprising, it was found that if this pigmentation was reduced in the final coat (to give a glossy finish), protection of the coating was also reduced (Section 9.3.1.5).

It was found that seasons had a pronounced effect on the rate of degradation. This was best displayed in the results obtained from DSC (Section 9.3.1), which showed disproportionate increases in the T_g during the summer months. This observation is confirmed by the DMTA results (when allowances are made to take into account the four month lag behind the DSC results). Thus, when the DMTA panels are initially exposed in December, there is the expected increase in the cross-link density (as observed in the reduction in height of the log tan δ plot), and then a further increase in cross link density after eight months (when the panel has been exposed for the summer, and withdrawn in August). This is accompanied by an increase in the stiffness of the coating above its T_g (as measured by the plot of the log of the storage modulus with temperature). The stiffness below the T_g, however, remains constant in the initial stages of exposure. Eventually, the cross-linking increases until the stiffness below the T_g has also increased.

10.2 Acrylics

As may be expected from a resin which is not intended to undergo any further cross-linking after application, there is little change in T_g, stiffness, nor IR spectra.

It was found in the DMTA results that after a period of natural weathering, acrylics increase their cross-linking density, whilst increasing the plasticisation of the film. This was evident in the plot of log tan δ with temperature for unexposed and exposed films. After sixteen months of natural exposure, the maximum value for log tan δ had been shifted down in height (indicating increased cross-link density) and to a lower temperature (indicating increased plasticisation).

A classical argument to explain this is that radical reactions are taking place, resulting in a more highly cross-linked matrix, but with lower molecular weight scission products. There are two arguments against this explanation. The first being that this change occurred in the winter or early spring months (i.e. between December and March), and radical reactions promoted by solar activity (the most common source during natural exposure) would be expected to be rarer than in the previous summer. The second argument lies in the fact that plasticising compounds were seen to remain constant or fall over this period.

It was hoped that changes in the infra-red spectrum would show changes in the surface of the paint, and also any extra compounds formed. It was found that the technique, when applied to coatings on wood, was not sensitive, nor reproducible enough to make such observations, for reasons already discussed (Section 9.4.5).

Another theory to explain this phenomenon has already been mooted (Section 9.3.2.2), and applied to the DMTA results. Restated simply, it requires that differing phases in the acrylic resin (whether due to differing molecular weight or chemical composition) become disassociated; forming an effectively more densely cross-linked matrix, and the other phase acting as a plasticiser.

The T_g of the acrylic resin used was between 5 and 12 °C. Between the months of December and March, a brown coating (such as both Systems 4 and 5) may be expected to cycle above and below its T_g owing to its high thermal gain in daytime, and cool nights. This process may aid a dissociation to occur.

The DMTA results have been shown to be consistent with this theory. At first, results obtained from DSC appear to conflict with the theory, as there is not a significant change in T_g over the winter/early spring months. DSC results are affected, in opposing ways, by both increasing molecular weight (in this theory due to the higher molecular weight portion) and increasing plasticising agents (the lower molecular weight material). As the two portions formed two parts of the original resin, it is not unreasonable that the two effects should cancel out.

10.3. Hybrid

The water-borne alkyd/acrylic hybrid used in this study showed results typical of its component resin types. There was an immediate increase in cross-linking, as observed in an increase in T_g and in a reduction in height of the maximum (due to the alkyd component) log tan δ against temperature plot. The DMTA results showed that the peak due to the alkyd component became so small due to additional cross-linking, that it was masked by the peak due to the acrylic component.

Although pigments have been shown to affect the three dimensional structure of alkyds, both on initial cross-linking, and photodegradation, this effect was not observed in this case. In the case of the “pure” alkyd (System 2), close examination of the log tan δ alkyd peak showed that it was a poorly resolved doublet, due to the two structures. Although the peak due to the alkyd component in the hybrid is broad, there is no indication that it contains more than one component. We cannot see if the structure has changed on extended exposure because the alkyd peak has been obscured by the acrylic peak after only eight months.

As with “pure” acrylics, there is little change in the T_g, nor in the IR spectrum (for reasons discussed in Section 9.4.5). Like the “pure” acrylics, the acrylic log tan δ peak is seen to change, although in this case after only twelve months (as opposed to the sixteen months for the other acrylic resin).

The nature of the change is, however, different. Here the coating becomes less cross-linked (as seen by an increase in the height of the log tan δ plot) but with a narrower range of molecular weights (effectively being less plasticised). With the “pure” acrylics, it was suggested that a separation of phases was taking place after a period during which the coating was cycled through its T_g. As the T_g for the hybrid at this stage lies between 12 and 18 °C, it is conceivable that such temperatures were attained between mid-October and December. The reason for shift to a less crosslinked matrix, with less plasticisation has already been discussed (Section 9.4.4) but lies in the predominant matrix being formed from a lower molecular weight material, with pockets of higher molecular weight material.

11. Conclusions

11.1. Alkyds (Systems 1, 2, 3, and 7)

Alkyds react with atmospheric oxygen, but it has been shown that these autoxidation reactions are influenced by a pigment (in this case iron oxide) to form a different polymeric structure from alkyds air dried in the absence of iron oxide. In the instance observed in this study, the new structure had a lower T_g, but similar cross-link density to those alkyds without iron oxide. This resulted in a dramatic decrease in the T_g observed by DSC, and two peaks (albeit not fully resolved) in the DMTA plot of the log tan δ versus temperature for the unexposed coating. One of these peaks was due to the "conventional" structure (occurring at the same temperature as the peak observed in the plots for the alkyds dried without iron oxide) and the other was due to the new structure.

Those paints with an alkyd component (i.e. both the solvent-borne "pure" alkyds and the water-borne alkyd-acrylic hybrid) increase their cross-link density within the first four months of natural exposure as seen by an increase in T_g and a lowering in the height of the DMTA log tan δ maximum point.

In the case for alkyds which had iron oxide as a pigment, the log tan δ maximum was also shifted on natural exposure, from the "conventional" value until only the new structure was detectable after sixteen months of natural exposure (for coatings initially exposed in December). The last statement should be read in the context that pigmentation has (as expected) been shown to have a net beneficial effect on the protection of coatings in general from photodegradation.

It was also found that disproportionate changes in the photodegradation of the coatings for all three resin types could be attributed to seasonal variations. For both coatings exposed in August (used in DSC studies) and those exposed in December (used for DMTA), there were more pronounced changes during summer months than for winter months. This was attributed to the increased solar activity promoting radical reactions.

11.2. Acrylics (Systems 4 and 5)

Those paints and varnishes with an acrylic component lose lower molecular weight material within four months of natural exposure. Additional material is not then lost for the remainder of the life of the coating. This can be attributed to the loss of additives (for example, the thickeners) and also low molecular weight oligomers. This observation was most clearly seen in the analysis for the non-polar non-volatile material. It is thought that the additives were not always extracted in the analysis for polar non-volatile material due to the additive being “bound” by the coating, possibly due to associative bonding.

It was found that coatings with an acrylic component separates after about 12 months into either a more highly cross-linked matrix with increased plasticisation, or a lower cross-link density matrix, with reduced plasticisation. This effect could not be seen by DSC and was only seen by DMTA on examination of the log tan δ versus temperature plot for the unexposed and exposed coatings. It was also noted that this phenomenon appeared to occur after seasons which would allow the coating to cycle through its T_g a number of times.

One theory which may explain this observation is that the range of molecular weights present in the resin is somehow separating out into high/low molecular weight fractions (possibly by a process akin to recrystalisation), and the predominant fraction is detected as the polymer backbone, with the other polymer matrix either plasticising (if of lower molecular weight) or reducing plasticisation (if of higher molecular weight).

11.3. Hybrid (System 6)

The hybrid studied exhibited trends similar to both “pure” alkyds and “pure” acrylics. It increased its cross link density on initial exposure in the same way as alkyds, and appeared to segregated into two phases in the same way as acrylics. In the case of the hybrid, this segregation was thought to be into a lower molecular material matrix, with “pockets” of higher molecular weight material.

12. Future Work

There are two main aspects of this work that I would like to see developed.

The first lies in the apparent ability of iron oxide to influence the autoxidation pathways of alkyds. This was apparent both in the initial curing reactions, and also as a result of photodegradation. I envisage that future work in this area would be two pronged, the first task being to establish other compounds (and especially pigments) which exhibit this phenomenon. As the iron oxide which exhibited these reactions was of the semi-transparent (i.e. very finely divided) variety it would be sensible to test whether other grades of iron oxide, or iron soaps (e.g. iron octanoate which should be soluble in an alkyd resin), also showed a similar trend.

When compounds which affect these reactions are identified, the next step must surely be to identify a mechanism for the process. This could involve incorporating iron (and any other elements) in a form of soaps (akin to driers - Section 4.1.1.3) into one or more alkyds, at differing concentrations. While it will be tempting, in an attempt to keep the final structure as simple as possible, to use a drying oil or even methyl linoleate, films so formed may be too weak to be studied by DMTA.

The second observation which I would like to see tested, is the apparent ability of acrylic resins to segregate into high/low molecular weight fractions. Such an investigation should include the thermal cycling of pigmented and unpigmented acrylics, before and after a period of natural exposure.

If areas of high molecular fractions do occur, and they behave like crystalline areas, they should be able to be observed using birefringence between crossed polarizers on a microscope[179]. Certainly, it would be interesting to investigate whether similar effects are observed for high molecular weight regions as is observed for crystalline regions[180].

13. References

1. Mechanism of Degradation of Wood Coating Systems, RR2/95, compiled by Falla, N. A. R., confidential to members of PRA, April 1995.
2. Surface Coatings Vol. 2-Paints and their applications, Oil and Colour Chemists' Association, Chapman & Hall (London), 1984, ISBN 0 412 26710 1, pp. 419-438.
3. Protective Coatings, Fundamentals of Chemistry and Composition, C. H. Hare, Technology Publishing Co. (Pittsburgh), 1994, ISBN 0-938477-90-0, pp. 1-13.
4. Feist, W. C. and Williams, R. S., American Paint and Coatings Journal, Vol. 76, No. 24, p38-48, 1991.
5. Boxall, J. and Smith, G. A., JOCCA, 12, pp 419-426, 1984.
6. Surface Coatings Vol. 1-Raw materials and their usage, Oil and Colour Chemists' Association, Chapman & Hall (London), 1993, ISBN 0 412 55210 8, pp. 76, 437-438, & 451.
7. Polymers: Chemistry and physics of modern materials, J. M. G. Cowie, International Textbook Co. Ltd (Aylesbury), 1973, ISBN 0 7002 0222 6, pp. 68-71.
8. Paint and Surface Coatings theory and practice, R Lambourne, Ellis Horwood Ltd (Chichester), 1987, ISBN 0-85312-692-5, pp. 111-193, 336,355, & 677.

9. Surface Coatings - 2, Edited by A. D. Wilson, J. W. Nicholson and H. J. Prosser, Elsevier Applied Science Publishers (London), 1987, ISBN 1-85166-194-8, pp. 183-223.

10. Airborne Pollutants in the Surface Coatings Industry, J. Moreton and N. A. R. Falla, Chemical Society Analytical Sciences Monograph (London), 1980, ISBN 0-85186-860-6, pp. 114-119.

11. Kronos Titanium Dioxide in Emulsion Paints, Dörr, H, and Holzinger, F, translated by Lyons, T and Münster, I, 1990.

12. BS 3900 Part G6, Assessment of resistance to fungal growth, 1989

13. BS 3900 Part H2, Designation of degree of blistering, 1983.

14. BS 3900 Part H4, Designation of degree of cracking, 1983.

15. BS 3900 Part H5, Designation of degree of flaking, 1983.

16. ASTM D3274 -82, Standard Test Method for Evaluating Degree of Surface Disfigurement of Paint Films by Microbial (Fungal or Algal) Growth or Soil and Dirt Accumulation, reapproved 1988.

17. BS 3900 Part F6, Notes for guidance on the conduct of natural weathering tests, 1976.

18. BS 3900 Part F3, Resistance to artificial weathering (enclosed carbon arc), 1971, amended 1979.

19. ASTM G 53, Standard Practice for Operating Light- and Water-Exposure Apparatus Fluorescent UV-Condensation Type) for Exposure of Nonmetallic Materials, 1993.

20. BS 3900 Part F14, Determination of resistance to artificial weathering by exposure to filtered xenon-arc radiation, 1995.

21. BS 3900 Part F4, Resistance to continuous salt spray, 1968, amended 1974 and 1979.

22. BS 3900 Part F2, Determination of resistance to humidity under condensation conditions, 1973.

23. BS 3900 Part F8, Determination of resistance to humid atmospheres containing sulphur dioxide, 1976.

24. The Care and Protection of Wood, Greystone, J., Published by ICI Paints Division (Slough), 1985, pp. 8,14,16-17, 24-27, 30-39, & 51.

25. Timber in Construction, Sunley, John, and Bedding, Barbara, B T Batsford/TRADA (London), 1985, ISBN 0713450533, page 13-15.

26. Timber in Construction, Sunley, John, and Bedding, Barbara, B T Batsford/TRADA (London), 1985, ISBN 0713450533, Appendix.

27. Noble, A. E., Miller, E. R., and Derbyshire, H., Construction and Building Materials, Vol. 9, No. 1, pp 3-11, 1995.

28. A Handbook of Softwoods, Ministry of Technology, Forest Products Research, HMSO (London), 1957, pp. 11-66.

29. Fox, B., world wide web site http://weber.u.washington.edu/~bfox/classic.html

30. Oxford Forestry Institute world wide web site, http://ifs.plants.ox.ac.uk/OFI/PUBS/OCCAS/45/CHEMICAL.HTM.

31. Miall's Dictionary of Chemistry, 5th edition, Sharp, D. W. A., Longman (Essex), 1981, ISBN 0 582 35152 9, p. 278 & 451.

32. Miller, E. R., and Boxall. J., Holz als Roh- und Werkstoff, No. 42, pp. 27-34, 1984.

33. Coatings for Wood. PRA Training Course. 10-11 March 1998.

34. Timber Its Structure and Properties, Desch, H. E., Macmillan (London), 1973, SBN 333 14890 8, pp. 66, 248-251, & 254-283.

35 Timber: Its Nature and Behaviour, Dinwoodie, J. M., Van Nostrand Reinhold Co. Ltd (Wokingham), 1981, ISBN 0-442-30445-5, p. 46.

36. The Chemistry of Solid Wood, Edited by Rowell, R. M., American Chemical Society (Washington) , 1984, ISBN 0-8412-0796-8, pp. 12-15, 240-241, & 401-451.

37. Miller. E. R., BRE News, No. 54, 15, 1981.

38. Derbyshire, H. and Miller, E. R., Holz als Roh- und Werkstoff, No. 39, pp 341-50, 1981.

39. Lindburg, B., VTT Symposium 49, Proc. 3rd Internat. Conf. on Durability of Building Materials & Components, Vol. 2, Espoo (Finland), pp 318-28, 1984.

40. Deglise, X. M., Dirckx, O. G., Masson, D. M. and Roux, M. L., ACS, Abs of Papers, 190th Meeting, Chicago 1985, Div. of Cellulose, Paper & Textiles, Abs 20.

41. Horn, B. A., Qiu, J., Owen, N. L. and Feist, W. C., Appl. Spectrosc., Vol. 48, No. 6, pp 662-8, 1994.

42. Derbyshire, H., Miller, E. R. and Turkulin, H., Holz als Roh- und Werkstoff, 53, pp 339-345, 1995.

43. Zerlaut, G. A. and Ellinger, M. L., J. Oil Col. Chem Assoc., Vol. 64, pp 387-397, 1981.

44. Hon, D. N-S., Appl. Polym. Symposia, No. 37, pp 845-64, 1983.

45. Hon, D. N-S and Chang, S-T, J. Polym. Sci, Polym Chem. Vol. 22, No. 9, pp 2227-41, 1984.

46. Derbyshire, H., Miller, E. R., Sell, J. and Turkulin, H., Drvna Industrija, Vol. 46, No. 3, pp 123-32, 1995.

47. Derbyshire, H., Miller, E. R. and Turkulin, H., Holz als Roh- und Werkstoff, 54, pp 1-6, 1996.

48. BS 2015, Glossary of Paint and related terms, 1992.

49. Falla, N. A. R., PRA Research Report RR2/95, Mechanism of Degradation of Wood Coating Systems, 1995, Confidential to members of PRA.

50. Falla, N. A. R., Proc. “Advances on Coatings Technology ACT ‘95” Conf., (Institute of Plastics & Paint Industry, Gliwice, Poland), Katowice (Poland), Paper 19, 15 pp, 1995.

51. Miller, R., PROC. PRA “Advances in Exterior Wood Coatings and CEN Standardisation” conf., Brussels, Paper 1, 16pp., 1998.

52. Bulian, F., Caon, C., Matellon, A., PROC. PRA “Advances in Exterior Wood Coatings and CEN Standardisation” conf., Brussels, Paper 3, 8 pp. 1988.

53. Falla, N A R et al, PRA Technical Report TR/1/91, Mechanism of Drying Part 1, Confidential to Members of PRA, 1991.

54. Falla, N A R et al, PRA Technical Report TR/1/91, Mechanism of Drying Part 2, Confidential to Members of PRA, 1991.

55. Falla, N A R et al, PRA Technical Report TR/1/91, Mechanism of Drying Part 3, Confidential to Members of PRA, 1991.

56. Fibres, Films, Plastics and Rubbers, Roff, W. J., Scott, J. R., The Butterworth Group (London), 1971, ISBN 0 408 15960 X, p 227-240.

57. An Introduction to Rheology, Barnes, H. A., Hutton, J. F., Walters, K., Elseivier Science Publishers B.V. (Amsterdam) 1989, ISBN 0-444-87140-3, pp. 11-35.

58. Prideaux, J, JOCCA, Vol. 76, No. 4, p177-182, 1993.

59. Shay, G., Bassett, D. and Rex, J. D., JOCCA, Vol. 76, No. 11, p446-452, 1993.

60. Shay, G, American Paint and Coatings Journal, Dec. 20 1993.

61. Basic Principles of Organic Chemistry, 2nd edition, Roberts, J. D., and Caserio, M. C., W A Benjamin Inc. (California), 1979, ISBN 0-8053-8322-0, pp. 803-805.

62. Textbook of Polymer Science, Billmeyer, F. W. Jr, John Wiley & Sons Inc. (New York) , 1962, Library of Congress Catalog Card Number 62-18350, pp. 343-344.

63. The RHEOVIS Manual, Allied Colloids Limited, Coatings and Specialities Division.

64. Hall, J. E., Hodgson, P, Krivanek, L and Malizia, P, Journal of Coatings Technology, Vol. 58, No. 738, pp 65-73, July 1986.

65. Springle, R et al, PRA Technical Report TR/4/87, Enzymatic Degradation of Emulsion Paint Thickeners, Confidential to Members of PRA, 1987.

66. Product Data sheet for Natrosol® Plus, Paint grade, Aqualon (UK) Limited.

67. Acrysol® Thickeners and Rheology Modifiers, A Selection Guide, Rohm and Haas Company.

68. Handbook of Coatings Additives, edited by Calbo, L. J., Marcel Dekker Inc. (New York) , 1987, ISBN 0-8247-7561-9, pp. 147-174 & pp. 511-539.

69. Cartridge, D. J., Double Liaison, No. 478, p70-73,1995.

70. Dispersion of Powders in Liquids, edited by Parfitt, G. D., Elseivier Publishing Co. Ltd (London), 1981, ISBN 0-85334-990-8, pp. 395-469.

71. Technical data sheet 5-2966, UCAR Polyphobe rheology modifiers, Union Carbide Company.

72. Ulyatt, J, 10th International Conference on Paint and the Environment (held at PRA), Paper 11, 1990.

73. Outlines of Paint Technology, third edition, Morgans, W. M., Edward Arnold (London), 1990, ISBN 0-85264-308-X, p.212-214.

74. Hofland. A. and Schaap, F., Polymer Paint and Colour Journal, Vol. 178, No. 4220, pp. 620-621, 1988.

75. Hofland, A., Pigment and Resins Technology, Vol. 23, No. 4, pp. 7-11, 1994.

76. Hofland, A., Surface Coatings International, Vol. 7, pp. 270-281, 1994.

77. Hofland, A.., Polymers Paint Colour Journal, Vol. 184, No. 4350, pp. 261-264, 1994.

78. Hofland, A., Polymers Paint Colour Journal, Vol. 184, No. 4353, pp. 350-354, 1994.

79. Hofland, A., Double Liaison - Physique, Chimie et Économie des Peintures et Adhésives, No. 471-472, pp. XIV-XXII, 1995.

80. Nabuurs, T., Baijards, R. A., and German, A. L., XXth International Conference in Organic Coatings, Science and Technology, Athens, Greece, July 4-8 1994.

81. Weger, W., Second Middle East Conference, organised by the Paint Research Association and held in Bahrain, 6-12 January 1995.

82. Weger, W., Polymers Paint Colour Journal, p 12-14, June 1995.

83. Derbyshire, H and Miller, E. R., Holz als Roh- und Werkstoff 39, p 341-350, 1981.

84. Derbyshire, H , Miller, E. R., and Turkulin, H., Holz als Roh- und Werkstoff 53, p339-345, 1995.

85. Derbyshire, H , Miller, E. R., and Turkulin, H., Holz als Roh- und Werkstoff 54, p1-6, 1996.

86. Derbyshire, H , Miller, E. R., Sell, J. and Turkulin, H., Drvna Industrija 46(3), p123-132, 1995.

87. Textbook of Physical Chemistry, Second Edition, Glasstone, S., Macmillan & Co. Ltd. (London), 1948, p. 1154-1188.

88. Physical Chemistry, Second Edition, Atkins, P. W., Oxford University Press, 1982, ISBN 0-19-855151-7, p. 952-955.

89. Polymer Photodegradation. Mechanisms and Experimental Methods, Rabek, J. F., Chapman & Hall (London), 1995, ISBN 0 412 58480 8, p1-50.

90. Polymer Photophysics and Photochemistry. An Introduction to the Study of Photoprocesses in Macromolecules, Guillet, J., Cambridge University Press (Cambridge), 1985, ISBN 0521 23506 5, p8-165.

91. Hare, C. H., Journal of Protective Coatings & Linings, p58-66, May 1992.

92. Hare, C. H., Journal of Protective Coatings & Linings, p69-76, July 1992.

93. Organic Coatings: Science and Technology, Volume II: Applications, Properties, and Performance, Wicks, Z. W. (Jr.), Jones, F. N., Pappas, S. P., John Wiley & Sons Inc. (New York), 1994, ISBN 0-471-59893-3, p. 132-152.

94. Mateo, J. L., Catalina, F., & Sastre, R., Revista de Plasticos Modernos, Núm. 391, p73-82, 1989.

95. Norrish, R. G. W., and Kirkbride, F. W., J. Chem. Soc., p.1518, 1932.

96. Kirkbride, F. W., and Norrish, R. G. W., J. Chem. Soc., p.119, 1933.

97. Norrish, R. G. W., Crone, H. G., and Saltmarsh, O., J. Chem. Soc., p. 1533, 1933.

98. Norrish, R. G. W., and Appleyard, M. E. S., J. Chem. Soc., p.874, 1934.

99. Norrish, R. G. W., Crone, H. G., and Saltmarsh, O., J. Chem. Soc., p. 1456, 1934.

100. Saltmarsh, O., and Norrish, R. G. W., J. Chem. Soc., p. 455, 1935.

101. Bamford, C. H., and Norrish, R. G. W., J. Chem. Soc., p. 1504, 1935.

102. Bloch, B. M., and Norrish, R. G. W., J. Chem. Soc., p. 1638, 1935.

103. Akeroyd, E. I., and Norrish, R. G. W., J. Chem. Soc., p. 890, 1936.

104. Carruthers, J. E., and Norrish, R. G. W., J. Chem. Soc., p. 1036, 1936.

105. Hirschlaff, E., and Norrish, R. G. W., J. Chem. Soc., p. 1580, 1935.

106. Bamford, C. H., and Norrish, R. G. W., J. Chem. Soc., p. 88, 1938.

107. Bamford, C. H., and Norrish, R. G. W., J. Chem. Soc., p. 1531, 1938.

108. Bamford, C. H., and Norrish, R. G. W., J. Chem. Soc., p. 1544, 1938.

109. Polymer Photophysics and Photochemistry. An Introduction to the Study of Photoprocesses in Macromolecules, Guillet, J., Cambridge University Press (Cambridge), 1985, ISBN 0521 23506 5, p261-293.

110. Chemical and Physical Changes in Paints or Painted Wood due to Ageing, Ahola, P., Technical Research Centre of Finland, VTT Publications (Finland), 1994, ISBN 951-38-4393-9, p.8-18.

111. Basic Principles of Organic Chemistry, 2nd edition, Roberts, J. D., and Caserio, M. C., W A Benjamin Inc. (California), 1979, ISBN 0-8053-8322-0, p.1380.

112. Polymer Photodegradation. Mechanisms and Experimental Methods, Rabek, J. F., Chapman & Hall (London), 1995, ISBN 0 412 58480 8, p.284-294.

113. Tsubouchi, K., and Doi, Y., Proc. Xvth International Conference in Organic Coatings Science and Technology, Athens, pp 431-61, 1989.

114. Hodson, J., and Lander, J. A., Polymer, Vol. 28, pp. 251-256, 1987.

115. Handbook of Chemistry and Physics, 33rd edition, Chemical Rubber Publishing Co. (Cleveland), 1951-1952, p.1324.

116. European Resin Directory 1995, European Resin Manufacturers Association (Redhill).

117. Crecelius, S. B., Kagarise, R. E., and Alexander, A. L., Industrial and Engineering Chemistry, pp. 1643-1649, 1955.

118. Polymer Photodegradation. Mechanisms and Experimental Methods, Rabek, J. F., Chapman & Hall (London), 1995, ISBN 0 412 58480 8, p134-146.

119. Rånby, B., J. M. S. - Pure Appl. Chem., A30(9 & 10), pp 583-594, 1993.

120. Comprehensive Polymer Science, Vol. 6, Chapter 18, Photodegradation, MacCallum, J. R., Pergamon Press plc (Oxford), 1989, ISBN 0-08-032515-7, p529-537.

121. Torikai. A., Ohno, M., and Fueki, K., Journal of Applied Polymer Science, Vol. 41, pp. 1023-1032, 1990.

122. Mitsuoka, T., Torikai, A., and Fueki, K., Journal of Applied Polymer Science, Vol. 47, pp. 1027-1032, 1993.

123. Lemaire, J., Gardette, J-L., and Lacoste, J., Makromol. Chem., Macromol. Symp., Vol. 70/71, pp. 419-431, 1993.

124. Rasti, F., and Scott, G., Studies in Conservation, 25, pp. 145-156, 1980.

125. Polymer Photodegradation. Mechanisms and Experimental Methods, Rabek, J. F., Chapman & Hall (London), 1995, ISBN 0 412 58480 8, p365-399.

126. Advanced Inorganic Chemistry. A Comprehensive Text. Fourth edition, Cotton, F. A., and Wilkinson, G., John Wiley & Sons Inc. (New York), 1980, ISBN 0-471-02775-8, pp. 692-708.

127. Handbook of Chemistry and Physics, 33rd edition, Chemical Rubber Publishing Co. (Cleveland), 1951-1952, p.1393.

128. Polymer Photodegradation. Mechanisms and Experimental Methods, Rabek, J. F., Chapman & Hall (London), 1995, ISBN 0 412 58480 8, p353-363.

129. Tang, L., Sallet, D., Lemaire, J., Macromolecules, Vol. 15, pp. 1437-1441, 1982.

130. Simpson, L. A., Australian OCCA Proceedings and News, Vol. 20, No. 5, pp. 6-10, 1983.

131. Simpson, L. A., Polymers Paint Colour Journal, Vol. 176, No. 4168, pp 408-415, 1986.

132. Polymer Photodegradation. Mechanisms and Experimental Methods, Rabek, J. F., Chapman & Hall (London), 1995, ISBN 0 412 58480 8, p399-409.

133. Synolac 6005W Technical data sheet, Cray Valley Products, March 1988.

134. Super Gelkyd 6006W Technical data sheet, Cray Valley Products, March 1988.

135. A Guide to Eastman Chemicals, Eastman Kodak Company, Publication P-160D. May 1986.

136. BS 6150, Code of Practice for Painting of Buildings, 1991.

137. Standardized Test Panels, Q Panel Company, USA, Data Sheet L-860A.

138. Yu, P. et al, Coatings World, Vol. 3, No. 6, p. 42, 1998.

139. De Wit, J. H. W., and Lenderink, H. J. W., Pitture Vernici, Vol. 74, No. 11, p. 45-48, 1998.

140. BS 3900 Part C5, Determination of film thickness, 1975.

141. Falla, N. A. R. et al, PRA Reference M0R1, Mechanism of protection of wood by modern surface coatings - Interim report July to December 1991, Confidential to members of PRA.

142. Falla, N. A. R. et al, PRA Reference M0R1, Mechanism of protection of wood by modern surface coatings - Summary report January to March 1992, Confidential to members of PRA.

143. Falla, N. A. R. et al, PRA Reference M0R1, Mechanism of protection of wood by modern surface coatings - Interim report January to June 1992, Confidential to members of PRA.

144. Falla, N. A. R. et al, PRA Reference M0R1, Mechanism of protection of wood by modern surface coatings - Summary report July to September 1992, Confidential to members of PRA.

145. BS 3900 Part E9, Buchholz indentation test, 1976.

146. Falla, N. A. R. et al, PRA Reference M0R1, Mechanism of protection of wood by modern surface coatings - Interim report July to December 1992, Confidential to members of PRA.

147. BS3900 Part E11, Bend test (cylindrical mandrel), 1985.

148. Fox, T. G. and Flory, P. J., J. of Applied Physics, Vol. 21, pp 581-591, 1950.

149. Flory, P. J., Journal of Polymer Science, Vol. 14, p315, 1954.

150. Rodriguez, F. and Long, T., J. of Polymer Sci., Vol. 44, pp 1281-1285, 1992.

151. Schmid, E. V., Polymer Paint Colour Journal, 180(4258), pp 212-217, 1990.

152. Richardson, M. J. and Savil, N. G., Polymer, 16, pp 753-757, 1975.

153. Richardson M. J., Analytical Proceedings, 17(6), pp 228-231, 1980.

154 Oosterbrock, M & de Vries, O. T., JOCCA, (10), pp 398-402, 1990.

155. Martin, P. B., Pitture Vernici, 65 (12), pp 13-20, 1989.

156. Richard, J., Polymer, 33 (3), pp 562-71, 1992.

157. Achorn, P. J. & Ferrillo, R. G., J. Appl. Polm. Sci., 54, 2033-44, 1994.

158. Skrovanek, D. J. & Schoff, C. K., Prog. Org. Coat., 16(2), 135-63, 1988.

159. Bratton, G. J., Wasson, E. A., Nicholson, J. W., and Wilson, A. D., JOCCA, Vol. 72, No. 1, pp. 10-14, 1989.

160. Encyclopaedia Britannica, University of Chicago (Chicago), 1993, ISBN 0-85229-571-5, p. 337, 341, & 906-907.

161. The Macmillan Family Encyclopaedia, Arete Publishing Company (Princeton), 1980, ISBN 0 333 29134 4, pp. 253-4.

162. An Infrared Spectroscopy Atlas for the Coatings Industry, Infrared Spectroscopy Committee, Chicago Society for Coatings Technology, DeSoto Inc. (Illinois), 1978, pp. 10-12.

163. Instrumental Methods of Analysis, Seventh Edition, Dean, J. A. and Settle, F. A., ISBN 0-534-08142-8, pp. 293-320, 1988.

164. 3200 Data Station Getting Started Manual, 091-0325D, Digilab Division.

165. Falla, N A R et al, PRA Code E1C2, Project 12 Surface Degradation of Polymeric Materials, Final Report, Confidential to Members of PRA, March 1995.

166. Handbook of Chemistry and Physics, 68th edition, CRC Press (Cleveland), 1987-1988, p. E-50.

167. Handbook of Chemistry and Physics, 54th edition, Chemical Rubber Publishing Company (Cleveland), 1973-1974, p. E-60.

168. Sato, K., Progress in Organic Coatings, 4, pp. 271-302, 1976.

169 Howard, G. J., and Shanks, R. A., J. Macromol. Sci. Vol. A17, No 2, pp 287-95, 1982.

170. Peyser, P., and Bascom, W. D., J. Macromol. Sci. - Pys., B13(4), pp. 597-610, 1977.

171. Peyser, P., Polym. - Plast. Technol. Eng., 10(2), pp. 117-129, 1978.

172 Thangavel, K., Subbi Reddy, M., and Yaseen, M., Paint & Resin, Vol. 57, No. 5, pp. 15-21 & 40, 1987.

173. Shareef. K. M. A., and Yaseen, M., Progr. Org. Coat. Vol. 13, No. 5, pp. 347-65, 1985.

174. Perera, D. Y., and Oosterbroek, M., Farg. Lack, Vol. 39, No. 6, pp. 148-52, 1993.

175. Winnik, M. A., Makromol. Chem. Macromol. Symposia, Vol. 52, pp. 327-43, 1992

176. Bianco, H., Cohen, Y., and Narkis, M., Progr. Colloid. Polym. Sci., Vol. 103, pp. 261-7, 1997.

177. O'Conner, K. M., and Orler, E. B., Proc. 14th Water-Borne & Higher Solids Coatings Symp., New Orleans, pp. 143-54, 1987.

178. Soltani, R., Laupretre, F., Monnerie, L., and Teyssie, P., Polymer, Vol. 39, No. 15, pp. 3297-309, 1998.

179. Textbook of Polymer Science, Billmeyer, F. W. Jr, John Wiley & Sons Inc. (New York), 1962, Library of Congress Catalog Card Number 62-18350, p158.

180. Polymers: Chemistry and physics of modern materials, J. M. G. Cowie, International Textbook Co. Ltd (Aylesbury), 1973, ISBN 0 7002 0222 6, pp. 184-201.