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Oxidation resistant coating

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Abstract

The invention relates to coating compositions for metal sheets and coils and the like which incorporate stabilising agents against oxidative damage.
The problem of arresting oxidative damage in resins and enhancing outdoor weathering performance of coatings is addressed by providing the coating with a resin cook antioxidant.

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COMPLETE SPECIFICATION

STANDARD PATENT

Applicant(s): BLUESCOPE STEEL LIMITED

Invention Title: "OXIDATION RESISTANT COATING"

The following statement is a full description of this invention, including the best method of performing it known to me/us:

Field of the Invention

The invention relates to coating compositions for metal sheets and coils and the like which incorporate stabilising agents against oxidative damage.

Background Art

Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

Coated metal sheets and coils are often exposed to harsh outdoor weathering conditions which can lead to the degradation of the coating composition over time. The degradation includes increased brittleness, loss of adhesion to the underlying steel substrate or primer (Delamination), cracking, chalking, loss of gloss and colour change, where applicable.

In order for coated metal sheets to be commercially viable, they need to exhibit good mechanical properties, such as coating hardness, adhesion and flexibility, and maintain these parameters at acceptable limits over extended periods of time when in use. Further, the coating must display good gloss and colour retention properties. Other properties, such as solvent resistance, are also desirable. The coating materials however need to be selected not just on the basis of their end use, but must meet the requirements of workability and processability in a cost effective manner.

Two of the main factors involved in the outdoor degradation of coated metal sheets and coils are believed to be UV radiation and thermal damage which result from outdoor exposure to sunlight. At the molecular level it is believed a significant mechanism responsible, among others, for the degradation of coatings is the presence of destructive oxidative processes which are initiated and propagated by light and heat. Solar radiation, oxygen, water, pollutants etc all contribute to the degradation, which is thought particularly severe in darker highly pigmented resins which attain a higher surface temperature under solar irradiation.

The problem of arresting oxidative damage in resins has been addressed previously by the addition of antioxidants into the resin mixture or into paint mixtures containing the resin. This approach however has not been highly successful. These methods have limited success in the short term but generally lose efficacy with time. It is believed that the lack of success is due in part to the fact that the antioxidant is mobile in the resin and can "bleed" or migrate from the resin, thus becoming ineffective. Antioxidants which have "bled" to the resin surface can themselves discolour quite badly.

Further, the antioxidants added in this way only produce a noticeable increase in oxidation resistance in polymers which have a naturally very low level of oxidation resistance as a result of their structure - polymers which may be defined as "low performance" in respect of their outdoor weatherability such as ROMP (ring opening metathesis polymers) polymers made from cyclopentadiene. These low performance type resins are typically used in applications such as wrapping films, which are produced very cheaply with entirely different end use characteristics in mind from coated coil products. A very important property of such low performance resins is their low cost, given their very short intended lifespan. These materials yellow easily and this is addressed by the addition of antioxidants, after formation. "High end performance" polymeric coatings, such as those suitable for outdoor use have a higher inherent degree of oxidation resistance than such low performance films. Simply adding antioxidants to the preformed "high end performance" resin based coating does not lead to a significant increase in the stability of the resin towards oxidatively mediated destruction.

The manufacturing and subsequent processing properties of the resins also need to be taken into account - for example, they should be capable of production at relatively high speeds, so they can be produced at a commercially viable price. For this reason, they should have rapid curing.

A number of documents are available which disclose the addition of antioxidants to resin precursor mixtures prior to the resin cook stage. However, it is not known in the prior art to test the actual weatherability of resins or resin-containing coating products in true outdoor weathering tests. Some documents describe accelerated weathering tests indoors, however such tests are not accurate predictors of long term stability outdoors as they tend to overstate the relative importance of UV light effects and greatly understate the effects of reaction with oxygen, thermal degradation, as well as thermal cycling. Further, the spectral distribution of radiation used in most accelerated UV tests does not replicate outdoor radiation. Consequently different degradation mechanisms occur in the accelerated tests, and correlation with outdoor performance is generally poor. In resins, the diffusion of species throughout the resin matrix can be a very slow process. The timescale of accelerated weathering studies (typically hundreds of hours) is insufficient to allow interaction of species which may be present in the resin matrix. Outdoor weathering tests are typically conducted over a number of years, which is several hundred times longer than accelerated weathering tests. The only way to determine in fact whether a resin is weather resistant is to actually allow sufficient time for any oxidative processes to occur.

Consistent with the notion that the prior art does not touch on the issue of long term weatherability is its focus on the retention of the single characteristic of whiteness or colourlessness of a paint or resin. Where antioxidants were added in the past, their purpose was to prevent yellowing of the resin. The prior art does not contemplate, much less suggest that antioxidants would have any stabilising effect beyond the prevention of initial yellowing. It was not thought in the past to add antioxidants to dark coloured or pigmented paints, despite the fact that these were known to degrade faster.

Indeed, darkly pigmented coatings are known to degrade at a significantly higher rate than corresponding coatings having a lighter colour. The present applicants have determined that for coatings applied to a steel insulated roof (ie, with no airflow behind the roof) a darkly pigmented coating (L value < 40) can rise to a temperature 30-40°C hotter than a corresponding light coloured (L value > 70) coating.

With un-insulated surfaces, with intermediately dark coatings (L value between 40-70) the temperature difference compared to a light colour can still be of the order of 20°C. Those skilled in the art will be aware of the general rule that for every ten degrees rise in temperature, the reaction rate is approximately doubled. This means that darkly pigmented surfaces can undergo degradative reactions at a rate up to sixteen times that of corresponding light coloured surfaces. However, because of the fact that yellowing in such dark coatings is unobservable, it has not previously been thought to pursue the possibility of improved outdoors weathering via resin cook antioxidant additions in such dark coloured coatings.

US 6251986 discloses the addition of resin cook antioxidants to acrylic resins which formed the basis for light coloured coatings and which subsequently underwent testing in an accelerated weathering machine. US 6001923 relates to the addition of resin cook antioxidants in unpigmented polyurethane resins and testing for physical and optical properties only.

US 5965256 relates to the use of fluorinated resins and US 5464909 to the use of polyester resins, while US 5376720 discloses the use of antioxidants in silicone based resins. These three documents deal respectively with clear coatings/accelerated weather testing, light coloured paints/accelerated weather testing and clear and light coloured coatings testing for mechanical properties. Such resins usually possess inherently good outdoor weatherabilites, believed to be as a consequence of their reduced numbers of reactive C-H bonds, these being replaced by C-F and Si-H bonds respectively. Fluorinated and silicone resins are generally , somewhat more limited in the range of monomeric precursors available to resin formulators compared to polyester resin monomers.

Polyester resins possess a number of specific advantages over other classes of resins. Because they are made from simple carboxylic acid and alcohol units, there is the possibility for the use of a large number of formulations and also these compounds can be manufactured relatively cheaply. When formulated into coatings polyesters can give a good balance of weatherability with mechanical properties.

US 5554701 and US 5097006 relate to the use of all-aliphatic or all-cycloaliphatic polyester resins. These two documents deal with light and/or clear coatings in accelerated weather tests. It is generally accepted that in order for resins to have sufficient hardness, the presence of a certain amount of aromatic residues is required. Polyester resins having exclusively aliphatic or cycloaliphatic moieties are generally not as stable for long term outdoor use. US 5397641 also pertains to light coloured coatings tested by accelerated weather machines.

On the other hand, it is possible to create much harder polyester resins, such as those of US 4680371, by the exclusive use of aromatic acid and aromatic alcohol (phenolic) components. All-aromatic polyesters result in hard resins, which are suitable for use in moulding or extrusion, which is a very different process from the coating applications which are the focus of the present invention. Harder resins also have reduced workability. US 4680371 discloses clear coatings and makes no suggestion of weather testing.

JP09286847-A discloses the use of an antioxidant specifically in the preparation of a white or clear coating but does not suggest that antioxidants can be used in the improvement of long term weatherability.

However, the present applicants have found that, unexpectedly, the addition of antioxidants to the resin precursor prior to the resin cook can also maintain the weatherability properties of dark or medium to dark pigmented polyester resins products which would not be considered to warrant the addition of antioxidant.

A "resin cook antioxidant" as herein defined is an antioxidant added to a resin precursor mixture prior to said resin precursor mixture being cooked to produce a high performance resin for improved outdoor weathering performance.

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

Description Of The Invention

According to a first aspect, the present invention provides a baked pigmented paint with an L value of less than 70 units when measured according to ASTM D2244 and having high outdoor weatherability and suitable for use in coated steel products, said baked pigmented paint including a high performance resin incorporating a resin cook antioxidant.

Preferably, the baked pigmented paint has an L value of less than 40 units when measured according to ASTM D2244.

Preferably, the baked pigmented paint has a gloss retention after 3 years outdoor exposure of at least 64%, and more preferably at least 75%, of the original gloss value as measured by AS1580.

Preferably, the baked pigmented paint has a colour change defined by a delta E when measured by ASTM D2244 of less than 1.23, and more preferably less than 0.2, after 3 years outdoor exposure.

Preferably the high performance resin is selected from the group consisting of fluorocarbons, polyesters, silicone polyesters, alkyds, acrylics, silicone acrylics,

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polyurethanes, polyester-urethanes, silicone alkyds and mixtures thereof. In one particularly preferred embodiment, the high performance resin is a polyester resin.

Preferably, the resin cook antioxidant is a primary antioxidant, a secondary antioxidant or mixtures thereof. One particularly preferred example of resin cook antioxidants are those secondary antioxidants selected from the group consisting of triphenylphosphite and tri(substituted-phenyl)phosphites. In an alternative preferred embodiment, the resin cook antioxidant is pentaerythrityl-tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate].

According to a second aspect the invention provides a pigmented paint composition suitable for coating onto steel and baking to provide a baked pigmented paint with an L value of less than 70 units when measured according to ASTM D2244 and having high outdoor weatherability, said paint including:

a pigment or pigment mixture selected to provide an L value of less than 70 after baking; and

a high performance thermosetting resin present in an amount of 40-60% by weight of the pigmented paint composition.

Preferably, the pigment or pigment mixture is selected to provide an L value of less than 40 after baking.

Preferably, the high performance thermosetting resin is present in an amount of 45-55% of unbaked paint, and more preferably in an amount of 50% by weight of the pigmented paint composition.

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Preferably, the pigment or pigment mixture is present in an amount of 15-25% by weight of the pigmented paint composition, and more preferably in an amount of 20% by weight of the pigmented paint composition.

Preferably the cross-linker is present in an amount of 5-10% by weight of the pigmented paint composition and preferably solvent is present in an amount of 10-40% by weight of the pigmented paint composition.

Preferably, the pigmented paint composition further includes one or more paint additives selected from the group consisting of catalysts desiccants, surfactants, antiblock agents, pH adjusters and thickeners.

The high performance resin is preferably selected from the group consisting of fluorocarbons, polyesters, silicone polyesters, alkyds, acrylics, silicone acrylics, polyurethanes, polyester-urethanes, silicone alkyds and mixtures thereof. More preferably, the high performance resin is a polyester resin

The pigment or mixture of pigments preferably include one or more members selected from the group consisting of titanium dioxide, ultramarine blue, phthalocyanine blue, phthalocyanine green, carbon black, black iron oxide, chromium green oxide, ferrite yellow and quindo red.

Preferably, the resin cook antioxidant is a primary antioxidant, a secondary antioxidant or mixtures thereof. One particularly preferred example of resin cook antioxidants are those secondary antioxidants selected from the group consisting of triphenylphosphite and tri(substituted-phenyl)phosphites. In an alternative preferred embodiment, the resin cook antioxidant is pentaerythrityl-tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate].

According to a third aspect, the invention provides a high performance thermosetting polyester resin incorporating a resin cook antioxidant and suitable for formulation into a baked pigmented paint with an L value of less than 70 units when measured according to ASTM D2244 and having high outdoor weatherability and suitable for use in coated steel products, said high performance polyester resin including:

an acid component set comprising diacids and/or triacids and/or monoacids and their anhydride analogues where applicable;
an alcohol component set comprising diols and/or triols and/or mono-alcohols; and a resin cook antioxidant.

A resin cook antioxidant is one which is added to the resin precursor mixture prior to the stage of cooking the resin.

Preferably, the acid component has 60-100 mole% of an aromatic acid, aromatic diacid, aromatic anhydride or mixtures thereof and 0-40 mole% of a non-aromatic acid, non-aromatic diacid, non-aromatic anhydride or mixtures thereof. More preferably, the acid component has 90-100 mole% of an aromatic acid, aromatic diacid, aromatic anhydride or mixtures thereof and 0-10 mole% of a non-aromatic acid, non-aromatic diacid, non-aromatic anhydride or mixtures thereof.

Preferably, the total alcohol component has a trihydroxy compound in an amount of 5 to 20 mole%, neopentyl glycol in an amount of 0 to 60 mole% and 40-95 mole% of a glycol selected from the group consisting of 2-butyl-2-ethyl-1,3-propanediol; neopentylglycol hydroxypivalate and glycols having a carbon atom β to a hydroxyl group mono- or di- substituted with a methyl, ethyl, propyl or butyl group(s).

It is also preferred that the high performance thermosetting polyester resin has equimolar amounts of acid and hydroxyl groups, an acid value in the range of 0 to 100, and more preferably 0 to 10, a hydroxy value in the range 20 to 110 and a number average molecular weight in the range 700 to 50000, and more preferably 700 to 8000.

Preferably, the trihydroxy compound is trimethylolethane or trimethylolpropane present in an amount of 10-20 mole% of the total alcohol component.

Preferably, the resin cook antioxidant is a primary antioxidant, a secondary antioxidant or mixtures thereof. One particularly preferred example of resin cook antioxidants are those secondary antioxidants selected from the group consisting of triphenylphosphite and tri(substituted-phenyl)phosphites. Triphenylphosphite is most preferred. In an alternative preferred embodiment, the resin cook antioxidant is pentaerythrityl-tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate].

Preferably the resin cook antioxidant is present in an amount less than 5% and more preferably in an amount of 0.01 to 2.0% by weight of the total resin.

The high performance thermosetting polyester may further include one or more of degassing agents, flow control agents and biocides.

The high performance resin may then be formulated into a paint in accordance with usual procedures and applied to a substrate such as a steel sheet or coil. Preferably, the resin is used in the preparation of pre-painted/pigmented coated steel for end use applications such as coil coatings, powder coatings, general industrial coatings, automotive coatings, gelcoats for outdoor use.

As herein defined, a high performance resin is one which is capable of having application as an outdoor use on coated steel and the like, with appropriate physical and mechanical properties. Such properties would be familiar to those skilled in the art and include, but are not limited to, being suitable for coating onto metal coil, the ability to be applied uniformly in a film thickness of 15 to 25 microns, a capacity for rapid thermal film cure, satisfactory film durability, flexibility, hardness, peel resistance, impact shock resistance and the like.

Examples of resins that can have high performance include fluorocarbons, polyesters, silicone polyesters, alkyds, acrylics, silicone acrylics, polyurethanes, polyester-urethanes, silicone alkyds and mixtures thereof.

Specifically excluded from the definition of high performance resins are those resins which are based around the polymerisation of norbornane or norbornane-like units, such as cyclopentadiene, dicyclopentadiene and the like, or resins which are involved in

ROMP (ring opening metathesis polymerisation) polymerisations. Such monomers and process produce polymers which traditionally are unsuited to the rigours of outdoor exposure. Epoxy resins, and in particular Bisphenol A type epoxy resins, are also not usually regarded as high performance resins.

The resins of the present invention are also noticeably less yellow in colour than resins produced by the previous methods in the art. In this regard, not only do the resins have superior resistance to oxidative destruction, but also commence from a position of having truer colour, and concomitantly, less impurities resulting from oxidative damage during cooking.

Preferably, the antioxidant was added prior to the preparation of an immediate precursor of said resin.

Thermosetting coatings are often used as decorative coatings for metal sheet coils. These coatings are typically produced by reacting at elevated temperatures a blend of hydroxyfunctional resin and a crosslinking agent such as a derivative of melamine formaldehyde, benzoguanamine formaldehyde, glycouril formaldehyde, urea formaldehyde or a blocked isocyanate resin. Hydroxyfunctional resins such as polyester, acrylic and alkyd are generally used as the major component of the decorative coatings and of those resins, polyesters are preferred.

Hydroxyfunctional polyester resins are generally manufactured by reacting glycols with a mixture of dicarboxylic acid components together with a trifunctional branching component to form a branched polyester. The mixture of dicarboxylic acid components comprises an aromatic dicarboxylic acid and an aliphatic dicarboxylic acid component. The aromatic dicarboxylic acid component may be, for example, orthophthalic acid, isophthalic acid, terephthalic acid and/or a corresponding anhydride and the aliphatic dicarboxylic acid component may, for example, be adipic, sebacic or succinic acid.

Generally, the acid component of the composition according to the present invention consists of 90 to 100 mole % of an aromatic acid, such as isophthalic acid and preferably from 95 to 100 mole % (based on the weight of the total acid component). The acid or anhydride component may also be substituted with one or more groups such as methyl, ethyl, butyl, propyl etc. However, groups that are prone to hydrolysis are generally not used and this makes the resulting coating composition more resistant to exterior exposure.

2-Butyl-2-ethyl-1,3-propanediol (BEPD) is the preferred glycol of the present invention as its esters do not readily hydrolyse, however other glycols such as neopentylglycol hydroxy pivalate (HPHP) may also be used as the glycol component. In one embodiment from about 0 to 20 mole % of neopentylglycol (NPG) on the total alcohol side of the formulation is used together with BEPD or neopentylglycol hydroxy pivalate and isophthalic acid. The glycols may also be derivatives that are generally resistant to hydrolysis. In particular they may be derivatives which contain carbon atoms beta to the hydroxyl substituents that are dialkylated where the dialkylated groups include but are not limited to methyl, ethyl, propyl, butyl etc.

The acid component and glycol component are mixed with suitable branching agents to provide the desired polyester composition. Useful polyester trifunctional branching agents include trimethylolpropane and trimethylolethane. Typically the trifunctional branching agent is present in an amount of from 0 to 20 mole % and more preferably from 10 to 20 mole % based on the total alcohol content.

The polyester resin generally has an acid value of from 0 to 10, a hydroxyl value of 20 to 110 and a number average molecular weight of from 700 to 8000.

Solvents, pigments, dispersants and catalysts can optionally be added to the thermosetting polyester resin and processed by conventional methods of manufacture to form a durable surface coating. Suitable pigments of the present invention include, but are not limited to, titanium dioxide, ultramarine blue, phthalocyanine blue, phthalocyanine green, carbon black, black iron oxide, chromium green oxide, ferrite yellow and quindo red.

Mechanism Of Oxidation

Without wishing to be bound by theory, the present applicant provides below a discussion of the mechanistic aspects of resin oxidation.

The exact mechanism of the oxidation of resins is dependent upon their exact chemical structure. For organic thermosetting coatings, two of the main classes of resins are the acrylics and the polyesters.

Oxidative degradation reactions take place in three broad phases: initiation, propagation and termination.

The general mechanisms of oxidation are discussed in texts such as "Additives for Coatings", 1986, Ch 8, P.J. Schirmann and Martin Dexter and shown below:

Starting material	→	$R^\cdot$	Initiation
$R^\cdot + O_2$	→	$ROO^\cdot$	Propagation
$ROO^\cdot + RH$	→	$ROOH + R^\cdot$	Propagation
$R^\cdot + R^\cdot$	→	R-R	Termination
$R^\cdot + ROO^\cdot$	→	ROOR	Termination
$ROO^\cdot + ROO^\cdot$	→	Aldehydes, Ketones	Termination

In both polyesters and acrylics, the rate limiting step is the initiation step. In the case of polyesters, and in particular isophthalate based polyesters, the main propagation step in oxidative destruction is believed to be thermal oxidation. In the case of acrylic based resins, the main propagation mechanism for oxidative destruction is believed to be photooxidation.

Thus, it is conceivable and has hitherto not been recognised, that the oxidative destruction reactions could in fact be occurring before the resin is even put in place onto the coating surface. For example, in the case of polyester resins, it is conceivable that the oxidative destruction process could be commenced during monomer production, resin cooking, long term resin and paint storage, or during the curing of a thermosetting resin or paint. By adding antioxidants at an early stage, i.e. prior to the resin cook, it is possible to reduce at very early stages in the resins life, indeed even as the resin is forming, the occurrence of oxidatively degradative reactions.

Because the increase in oxidised polymer species concentration with time is a logarithmic type function, the earlier in the polymer oxidising lifetime one can inhibit the oxidation process, the more effective the delay in oxidatively induced degradation per unit outdoor weathering exposure time. For this reason, in accordance with the present invention, it is also possible to add antioxidants even earlier than the resin cook stage, namely, during the preparation of resin precursor components.

A similar situation applies, but to a lesser extent to other resins, including acrylic resins.

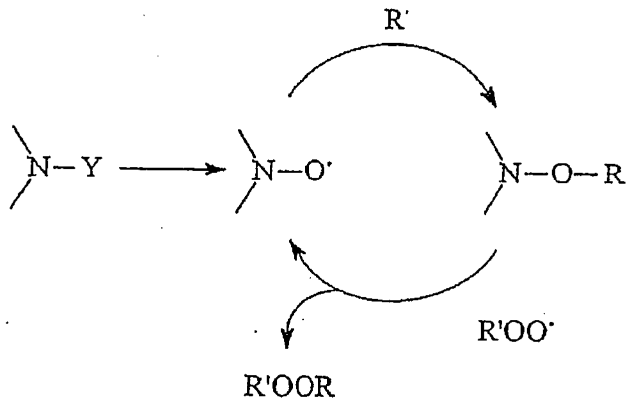
The antioxidants suitable for use in the present invention fall into two broad classes - primary antioxidants and secondary antioxidants.

Primary antioxidants are those which interrupt the oxidation chain reaction by reacting with active radicals to produce stable, less active radicals, and are typically phenolic type antioxidants, or amine type antioxidants. Usually, to prevent side reaction, these species are sterically hindered phenols or hindered amine light stabilisers (HALS).

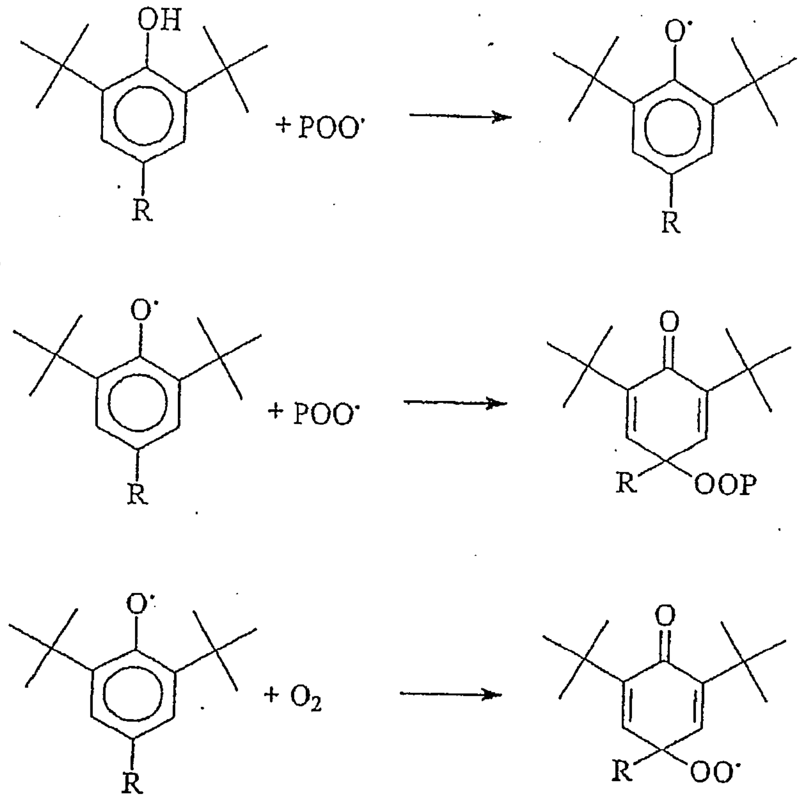
Hindered amines act as photosensitizers by trapping alkoxy and hydroxy radicals produced by the light induced dissociation of hydroperoxides. The hindered amines provide continuing resistance against photodegradation because they produce hydroxylamines and nitroxyl radicals, such as is shown in the scheme below. A nitroxyl radical is an example of a radical scavenger and is capable of catalytically consuming degradative species.

The cyclic mechanism shown below is known as the Denisov cycle and is thought to explain the long term effectiveness of hindered amines and the nitroxyl radicals derived from them. This is important, because even given this high ongoing efficacy, the cost of HALs is high and is a significant factor to be considered.

The amount of nitroxyl radical present in a resin has been correlated with the effective concentration of active HALS.



Hindered phenols act by a different mechanism , shown below, but still target active radicals.



Secondary antioxidants, by contrast, are those which react with peroxides to form stable products. These include for example, phosphorous acid esters, sulphides, disulphides, xanthates and dithiocarbamates. Their mechanism of action is shown below

$$ROOH + S(R')(R'') \longrightarrow ROH + O{=}S(R')(R'')$$

$$ROOH + P(OR')_3 \longrightarrow ROH + O{=}P(OR'_3)$$

Although such secondary antioxidants are stoichiometric, rather than catalytic, they are cheap and as such are a reasonably cost effective way of protecting coatings from UV damage.

It will be appreciated that the antioxidants chosen need to be stable in the reaction conditions in which they are used. Clearly, a greater range of antioxidants are available for use in low temperature process than would be available for high temperature processes. The antioxidants also need to be selected with regards to their chemical compatibility with the other components of the mixture.

In giving some examples below of primary and secondary anti-oxidants the following should be borne in mind:

(i) for elevated temperature polymerisations above 100-150°C only the heat stable examples from the groups mentioned below would be applicable. Whereas this would not be a restriction for low temperature solution polymerisation up to for example 70-80°C in the case of say one type of polyarylate polyester production.

(ii) for free radical polymerisation derived polymers eg acrylics, those anti-oxidants that can interfere with the free radical process are to be avoided, particularly the primary anti-oxidant type.

Antioxidants suitable for use in the present invention include, but are not limited to primary antioxidants, such as the following phenolic antioxidants:

p-hydroxyphenylcyclohexane, Bis(*p*-hydroxyphenyl)cyclohexane, 1,1-Bis(*m*-cresyl)propane, 1,1,3-Tris(2-methyl-4-hydroxy-5-*tert*-butylphenyl)butane, Tetra-tris-methylene-3-(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)propionate methane, 2,6-Di-*tert*-butyl-4-methyphenol, 2,4,6-Tri-*tert*-butylphenol, 1,1'-Methylene-bis(4-hydroxy-3,5-*tert*-butylphenol), 2,2'-Methylene-bis(4-methyl-6-*tert*-butylphenol), 2,6-(2-*Tert*-butyl-4-methyl-6-methylphenol-*p*-cresol), 1,4'-Butylidene (6-*tert*-butyl-*m*-cresol), Phenylethylpyrocatechol, Phenylisopropylpyrocatechol, 2,2'-Thiobis(4-methyl-6-*tert*-butylphenol) and 4,4'-Thiobis(3-methyl-6-*tert*-butylphenol).

Butylated phenols, butylated Cresols, 2,2-Methylene-bis(4-methyl-6-tert-butyl)phenol, Butylated hydroxy anisole (BHA), Butylated hydroxy toluene (BHT), 2,5-Di-tert butylhydroquinone, Hydroquinone monomethyl ether, Hydroquinone, 2,6-di-tert butylphenol, 2,6-di tert butyl-4-sec-butylphenol, 2,6-di tert butyl-4-nonylphenol, Mono-tertbutyl hydroquinone, p-benzoquinone, 2,4-dimethyl-6-tertbutyl phenol, methytlhydroquinone and 1,1,3 tris (2-methyl-4-hydroxy-5-t-butyl phenyl)-butane may also be used.

The following Primary antioxidants from the amine class may also be used: Diphenylamine, Phenyl-α-naphthylamine, Phenyl-β-naphthylamine, *N,N'*-Diphenyl-p-phenylenediamine, *N,N'*-phenylcyclohexyl-p-phenylenediamine, *N,N'*-(di-β-naphthyl)-p-phenylenediamine, Bis(2,2,6,6,-tetramethyl-4-piperidinyl)sebacate, Bis(1,2,2,6,6,-pentamethyl-4-piperidinyl)sebacate, Bis(1-octyloxy-2,2,6,6,-tetramethyl-4-piperidinyl)sebacate, Bis (1,2,2,6,6,-pentamethyl-4-piperidinyl)[3,5bis(1,1-dimethylethyl-4-hydroxypenyl)methyl]butylpropanedioate, 8-Acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazasprio(4,5)decane-2,4-dione, Dodecyl/tetradecyl-3-(2,2,4,4-tetramethyl-21-oxo-7-oxa-3,20-diazadispiro(5.1.11.12)henicosan-20-yl)propionate, N-(1,2,2,6,6-pentamenthyl-4-piperidinyl)-2-dodecylsuccinimid, N-(1-Acetyl-2,2,6,6-tetramethyl-4-piperidinyl)-2-dodecylsuccinimid, N-(2-hydroxyethyl)-2,6,6,6-tetramethylpipidin-4-ol-succinic acid copolymer and 1,3,5-Triazine-2,4,6-triamine,N, N'''-{1,2-ethandiylbis[[[4,6-bis[butyl(1,2,2,6,6-pentamentyl-4-piperidinyl)amino]1,3,5-triazin-2-yl]imino]-3,1-propandiyl]]bis[N, N'''-dibutyl-N',N'''-bis(1,2,2,6,6-pentamethyl-4-piperidinyl)] Poly-{[6-[(1,1,3,3-tetramethylbutyl)-amino]-1,3,5-triazin-2,4,-diyl][(2,2,6,6-tetramethylpiperidinyl)imino]-1,6-hexan-diyl[(2,2,6,6-tetramethyl-4-piperidinyl)-imino]}

Compounds such as Methyl ethyl ketoxime and Cyclohexanone oxime can also be used.

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The following secondary antioxidants may also be used: Dilauryl thiodipropionate, Distearyl thiodipropionate, Triphenyl phosphite, Tris(nonylphenyl) phosphite, Tris(mixed mono- and di- nonylphenyl) phosphite, Phenyl benzyl sulfide, Tetramethyl thiuram monosulfide, Tetramethyl thiuram disulfide, 2,2'-Diphenyldiamine disulfide, 4,4'-Diphenyldiamine disulfide, Mercaptobenzimidazole, Dodecylmercaptan, Xanthates, Dithiocarbamates, Dioctadecyl disulfide

The invention can be used with any resin which is used or useful in thermosetting coatings for application to coated steel products. These have been defined herein as high performance resins suitable for outdoor use with good gloss and colour retention.

These include, but are not limited to, polyesters, silicone modified polyesters, acrylics, silicone modified acrylics, glycourils, polyvinylidene fluoride/acrylic resins and cross linking resins. Cross linking resins include the melamine-formaldehyde benzoguanamine formaldehyde, glycouril formaldehyde, urea formaldehyde or blocked isocyanate resins.

The final paint mixture may contain pigments. Indeed, it is anticipated that the benefits of the present invention would be displayed most prominently under those circumstances where a dark pigment was included in the coating. The reason for this is that a darkly pigmented resin will have a significantly higher heat absorption and consequently a higher exposed service temperature compared to a light coloured resin, and so the rate of thermal oxidation would be much higher. However, the present invention is applicable for all colours and even for colourless resins. Suitable pigments include ceramic pigments, inorganic pigments, mixed metal oxide pigments and others known to those in the art.

The resins of the present invention may also include more than one additive to combat oxidative damage, extra additive examples being UV light absorbers (UVLA) and HALS, added either before resin cooking or added particularly subsequently, to enhance the activity of the resin cook antioxidants of the present invention. For example, a known UV absorber screens out a lot of UV light which damages the resin. These known UV absorbers break down over time but can provide an extra layer of defence against gloss loss and colour fading. Their breakdown may in turn be slowed by the addition of the resin cook antioxidants of the present invention, thus providing a synergistic enhancement of protection against oxidation.

Preferably, the antioxidant is added in an amount up to 1% of the total resin mixture, and preferably in the range 0.1 to 1.0%, depending upon the exact species used although it has been found that concentrations under 5% will not affect resin processing. There would be little need to exceed 5% antioxidant in the resin. In the literature concentrations as low as 0.01 to 0.02% are reported to be an effective amount for the triphenyl phosphite antioxidant used in a related way.

The antioxidants are powdered where solid and are added just prior to the melt stage.

It has been noted that when preparing resins by the present method, the resins are colourless or virtually colourless to the eye, by comparison with normal resin which usually present a slightly yellow appearance. In this regard, the resins of the present invention are less oxidised and give a much better starting point for the resin's subsequent outdoor weathering.

It was observed that, following the weathering tests, the paints prepared from resins containing resin cook antioxidants retained higher levels of gloss and colour retention than either an identical high performance resin without antioxidant, or a current commercial topcoat paint system with the same generic base resin system type (=control). These results are shown in the figures and are discussed in more detail below in the examples.

Figure 1 shows gloss retention as a function of time.

Figure 2 shows colour retention as a function of time.

Other resin additives include surfactants, catalysts, flatting agents and biocides

Best Method of Performing the Invention

Example 1. Resin Raw Materials.

Table 1 shows a number of examples of resin formulation of the present invention. Shown are the amounts and molar quantities of the components. The catalyst used was to assist the esterification reaction used to form the polyester resin.

Example 2. Visual Description of Resins.

Table 2 shows the visual appearance of unpigmented resins of the present invention. All 100% solids resins were hard solids at room temperature of 25°C. To obtain a 60% solids resin solution, the resin was dissolved in Solvesso 150 solvent.

Overall, the order of increasing colour in the resins was: Resins 2, 3, 5 least coloured, resin 8 slightly more coloured but nearly colourless, resin 7 very pale yellow but still nearly colourless, resin 1 very pale yellow and resins 4, 6 and control most highly coloured.

Example 3. Resin cook.

Table 3 shows a typical example of a resin cook according to the present invention. All resin cooks of the material in table 1 were carried out in accordance with this procedure. The results obtained were very similar.

The particular example given is for resin number 1 from the previous tables. However, all other resin cooks were very similar because the monomer set was the same each time, with variations being only in the type & level of anti-oxidant additive used

Monomer types & masses for resin 1, from table 1, were charged into a 1 litre glass reaction flask with ports for a nitrogen gas blanket, flame proof stirrer, thermocouple temperature probe, condensation apparatus and one port for the addition of any extra materials like xylene. The target acid value for this resin was 3, which gave a certain expected water of esterification, number average molecular weight, hydroxyl value & theoretical average acid & hydroxyl functionality per molecule

The units for Nitrogen flow rate of gas blanket are L/minute/L of cooking vessel headspace. The actual water of esterification captured was less than the theoretical expected because of some losses via the condensation apparatus (i.e. captured 44mL out of theoretical 61.1mL). In all cases, xylene was added to the melt as an azeotroping solvent for the water of esterification

Example 4. Paint Compositions

The resin numbering in Table 4 refers to those resins detailed in Table 1. The paint components were sourced as follows: Shepherd pigments from The Shepherd Colour Company, Ohio, USA; Rutile R960 titanium dioxide from DuPont; Aerosil R972 from Degussa; Cymel 1156 & Cycat 600 from Cytec Industries Inc (formerly American Cyanamid Company); DMEA = N,N-dimethylethanolamine from Sigma-Aldrich; Byk 306 from Byk Chemie GmbH; Syloid ED-5 from WR Grace; Solvesso 150 from Exxon-Mobil.

The pigment combinations referred to in Table 4 gave a similar dark brown colour.

It is expected that the present invention has particular applicability in the cases of dark pigmented paints. Dark paints are those which have a colour, after baking, as defined by "L Values" of an L value of less than 40 units. The L value comes from the L, a, b colour scale as per US standard ASTM D2244.

Example 5. Application and Baking of Topcoats.

Topcoats were applied on epoxy primed AZ150 G300 (AS1397) ZINCALUME coated sheet steel with a steel substrate thickness of 0.55mm. Topcoat dry film thicknesses of 18 microns were targeted after the bake cycle of 52s to a PMT of 232°C for the current commercial control (= topcoat paint system with the same generic base resin systems type), and 64s to a PMT of 245 degC for the other paint systems.

Example 6. Gloss and Colour Retention Tests.

The requirements for resistance to colour change and for good gloss retention when exposed to weather are difficult to satisfy and present a particular problem because data obtained by means of a UV-A accelerated weatherometer does not always correlate well with data from a UV-B accelerometer and both can correlate poorly with actual outdoor weather exposure. Sample resins which "pass" in the weatherometer sometimes "fail" on exposure to weather and sample resins which fail in the weatherometer are frequently rejected without further testing. The best way to test outdoor weathering is in actual outdoor conditions.

The Exposure site was located near Rockhampton, Queensland, Australia with panels exposed at an angle of 45 degrees from the horizontal facing due North.

The dark brown topcoats tested were the 10 paints (this includes one internal control) listed in Table 4 along with two commercial controls

Gloss retention is defined as a percentage of the original unweathered gloss retained. The exact conditions and manner of obtaining such a percentage figure from the raw glossmeter data are according to AS1580.602.2(1994) at an angle of 60 degrees from the normal.

Colour measurements were carried out according to ASTMD2244,using an instrumental colour spectrophotometer, such as a Datacolour Dataflash 100 spectrophotometer. Colour retention is defined in terms of the change in colour intensity, ΔE. Broadly speaking, a zero value for ΔE corresponds to no colour change, while a large ΔE corresponds to a poor colour retention.

Example 7. Results.

Table 5 shows the results of the gloss and colour retention tests for all the paints tested each year up to and including 5 years at Rockhampton. Tables 6 and 7 extract the data for paint 5, one of the best performing paints, compared to the controls, which is plotted in Figs 1 and 2, which plot gloss retention v exposure time and colour change v exposure time.

TABLE 1: RESIN RAW MATERIAL COMPONENT TABLE

Resin Number	Monomer Composition							Catalyst	Anti-oxidant and/or Other Additive			
	BEPD Mass (g)	BEPD Moles	TMP Mass (g)	TMP Moles	IPA Mass (g)	IPA Moles	Total Monomer Mass (g)	Fascat 4100 (g)	First Component	Mass (g)	Second Component	Mass (g)
1	251.1	1.57	28.1	0.21	281.9	1.7	561.1	0.56	TPP	0.56		
2	251.1	1.57	28.1	0.21	281.9	1.7	561.1	0.56	TPP	5.6		
3	251.1	1.57	28.1	0.21	281.9	1.7	561.1	0.56	I168	5.6		
4	251.1	1.57	28.1	0.21	281.9	1.7	561.1	0.56	I1010	5.6		
5	251.1	1.57	28.1	0.21	281.9	1.7	561.1	0.56	I168	2.8	I1010	2.8
6	251.1	1.57	28.1	0.21	281.9	1.7	561.1	0.56	I1010	5.6		
7	251.1	1.57	28.1	0.21	281.9	1.7	561.1	0.56	TPP	2.8		
8	251.1	1.57	28.1	0.21	281.9	1.7	561.1	0.56	TPP	0.57	Phos. Acid	0.701
Control	251.1	1.57	28.1	0.21	281.9	1.7	561.1	0.56				

Notes for Table:

(1) BEPD = 2-butyl-2-ethyl-1,3-propanediol from Eastman Chemicals, CAS [115-84-4]
(2) TMP = trimethylolpropane or 2-ethyl-2-(hydroxymethyl)-1,3-propanediol ; From Aldrich Chemical Co. ; CAS [77-99-6]
(3) IPA = Isophthalic Acid; From Aldrich Chemical Co. ; CAS [121-91-5]
(4) Fascat 4100 = mono butyl tin oxide ; From M&T Chemicals Inc. at the time.
(5) TPP = triphenyl phosphite ; From Aldrich Chemical Co. ; CAS [101-02-0]
(6) Phos. Acid = 81%w/w phosphoric acid; From BDH-Merck; CAS [7664-38-2]
(7) I168 = Irgafos 168 = tris (2,4 - di tert butyl phenyl) phosphite ; From Ciba-Geigy; CAS [31570-04-4]
(8) I1010 = Irganox 1010 = Pentaerythrityl - tetrakis [3 - (3,5 - di tert butyl - 4 - hydroxyphenyl) - propionate] ; from Ciba-Geigy CAS [6683-19-8]

TABLE 2: RESIN VISUAL APPEARANCE

Resin Number	VISUAL APPEARANCE			
	As 100% Solids Resin		As c 60% Solids Resin Solution	
	Colour	Clarity	Colour	Clarity
1	Very Pale Yellow	Clear		
2	Nearly Colourless	Slightly Milky Significant entrapped air bubbles	Nearly Colourless	Slightly Milky
3	Nearly Colourless	Slightly Milky Significant entrapped air bubbles	Nearly Colourless	Clear
4			Pale Yellow	Clear
5	Nearly Colourless	Slightly Milky Significant entrapped air bubbles	Nearly Colourless	Very slightly Milky
6	Yellow	Clear with Significant entrapped air bubbles	Yellow	Clear
7	Very Pale Yellow to nearly colourless	Slightly Milky Significant entrapped air bubbles	Very Pale Yellow to nearly colourless	Slightly Milky
8	Nearly Colourless	Slightly Milky Significant entrapped air bubbles	Very Pale Yellow to nearly colourless	Clear
Control	Pale Yellow-Straw	Clear	Pale Yellow-Straw	Clear

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TABLE 3: EXAMPLE OF TYPICAL RESIN COOKING LOG - FOR RESIN 1

Resin Cooking Time (hours)	Temperature of melt (degC)	Water of esterification evolved (mL)	Acid Number	Nitrogen flow rate of gas Blanket	Comments
0	20	0		0.2	All monomers & anti-oxidant charged to vessel
0.25	34	0		0.2	Monomers starting to melt
0.33	48	0		0.2	20mL xylene added
0.65	94	0		0.2	
1	150	0		0.2	Starting to reflux
1.25	164	0		0.2	15mL xylene added
1.5	180	0		0.2	
2.2	190	2.5		0.2	Steady reflux rate
2.6	190	9.5		0.2	
3	190	17.5		0.2	
3.66	210	22.5		0.2	
4.15	212	28		0.2	
4.77	215	33		0.2	
4.88	215	33		0.2	5mL xylene added
5.23	215	36		0.2	
6.33	215	36	37.9	0.2	
7.33	204	40		0.2	10mL xylene added
7.83	230	41		0.2	10mL xylene added
8.37	216	44		0.2	
8.58	216	44	13.7	0.2	
9.83	216	44	6.9	0.2	
11.24	220	44	4.5	0.2	
12.5	220	44	2.5	0.2	
12.83	230	44		0.2	Xylene flash off begun with condensation apparatus off
14.33	230	44		0.2	Heat turned off for melt cool down

TABLE 4: DARK BROWN PAINT FORMULATIONS

Paint Component	Paint Numbers [component masses (g)]									
	1 (Using resin solution 1)	2 (Using resin solution 2)	3 (Using resin solution 3)	4 (Using resin solution 4)	5 (Using resin solution 5)	6 (Using resin solution 2)	7 (Using resin solution 5)	8 (Using resin solution 7)	9 (Using resin solution 8)	10 (Using control resin solution)
Shepherd Brown # 39	35.07	35.07	35.07	35.07	27.16	8.77	8.77	8.77	8.77	38.20
Shepherd Black # 1	22.89	22.89	22.89	22.89	17.73	5.72	5.72	5.72	5.72	24.93
Shepherd Yellow # 195	15.87	15.87	15.87	15.87	12.30	3.97	3.97	3.97	3.97	17.29
Rutile R960	6.42	6.42	6.42	6.42	4.97	1.61	1.61	1.61	1.61	6.99
Aerosil R972	1.61	1.61	1.61	1.61	1.24	0.40	0.40	0.40	0.40	1.75
Polyester Resin Solution	208.17	280.09	186.99	221.60	173.72	68.67	54.98	56.14	56.14	221.72
Cymel 1156	32.63	32.63	32.63	32.63	25.28	8.17	8.17	8.17	8.17	36.41
Cycat 600	0.91	0.91	0.91	0.91	0.71	0.23	0.23	0.23	0.23	0.99
DMEA	0.19	0.19	0.19	0.19	0.15	0.05	0.05	0.05	0.05	0.21
Byk 306	0.76	0.91	0.71	0.78	0.61	0.22	0.19	0.19	0.19	0.83
Syloid ED-5	13.23	15.84	12.46	13.71	10.70	2.20	1.92	1.94	1.94	14.50
Solvesso 150	61.62	75.39	81.82	62.72	44.08	41.97	21.23	40.43	21.03	52.36
TOTALS	399.36	487.81	397.57	414.41	318.64	141.97	107.23	127.62	108.22	416.18

TABLE 5: OUTDOOR WEATHERING RESULTS AT ROCKHAMPTON

Test Paint	Rockhampton Exposure Results										
	Initial Gloss (unexposed)	Year 1		Year 2		Year 3		Year 4		Year 5	
		% Gloss Retention	Delta E	% Gloss Retention	Delta E	% Gloss Retention	Delta E	% Gloss Retention	Delta E	% Gloss Retention	Delta E
Paint 1	12	92	0.37	92	0.55	75	0.12	50	0.21	25	2.19
Paint 2	8	88	0.26	88	0.55	75	0.33	63	0.29	38	0.79
Paint 3	11	100	0.39	91	0.15	73	0.44	55	0.45	27	2.02
Paint 4	14	93	0.11	86	0.27	64	0.24	50	0.49	21	2.42
Paint 5	15	93	0.11	87	0.39	73	0.2	60	0.47	33	1.69
Paint 6	37	130	0.41	103	0.17	95	1.23	68	0.73	22	5.45
Paint 7	38	132	0.27	100	0.29	87	1.23	66	0.39	32	4.57
Paint 8	31	135	0.21	103	0.15	77	1.14	48	1.47	13	5.12
Paint 9	36	142	0.27	100	0.24	86	1.17	69	0.32	33	4.36
Internal Control	27	93	0.12	81	0.5	59	0.89	37	1.45	7	3.57
Commercial Control - 1	23	57	1.1	22	1.43	9	1.68	4	1.55	4	1.95
Commercial Control - 2	24	46	1.48	29	2.12	4	3.99	0	5.63	4	6.34

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TABLE 6 GLOSS RETENTION EXAMPLE GRAPH USING PAINT 5 & CONTROLS

Years Exposure	0	1	2	3	4	5
Paint 5	100	93	87	73	60	33
Internal Control	100	93	81	59	37	7
Commercial Control - 1	100	57	22	9	4	4
Commercial Control - 2	100	46	29	4	0	4

TABLE 7 COLOUR CHANGE EXAMPLE USING PAINT 5 AND CONTROLS

Years Exposure	0	1	2	3	4	5
Paint 5	0	0.11	0.39	0.2	0.47	1.69
Internal Control	0	0.12	0.5	0.89	1.45	3.57
Commercial Control - 1	0	1.1	1.43	1.68	1.55	1.95
Commercial Control - 2	0	1.48	2.12	3.99	5.63	6.34

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THE CLAIMS OF THE INVENTION ARE AS FOLLOWS:

1. A baked pigmented paint with an L value of less than 70 units when measured according to ASTM D2244 and having high outdoor weatherability and suitable for use in coated steel products, said baked pigmented paint including a high performance resin incorporating a resin cook antioxidant.

2. A baked pigmented paint according to claim 1 with an L value of less than 40 units when measured according to ASTM D2244.

3. A baked pigmented paint according to any one of the preceding claims having a gloss retention after 3 years outdoor exposure of at least 64% of the original gloss value as measured by AS1580.

4. A baked pigmented paint according to any one of the preceding claims having a gloss retention after 3 years external exposure of at least 75% of the original gloss value as measured by AS1580.

5. A baked pigmented paint according to any one of the preceding claims having a colour change defined by a delta E when measured by ASTM D2244 of less than 1.23 after 3 years outdoor exposure.

6. A baked pigmented paint according to any one of the preceding claims having a colour change defined by a delta E when measured by ASTM D2244 of less than 0.2 after 3 years outdoor exposure.

7. A baked pigmented paint according to any one of the preceding claims wherein the high performance resin is selected from the group consisting of fluorocarbons, polyesters, silicone polyesters, alkyds, acrylics, silicone acrylics, polyurethanes, polyester-urethanes, silicone alkyds and mixtures thereof.

8. A baked pigmented paint according to claim 7 wherein the high performance resin is a polyester resin.

9. A baked pigmented paint according to any one of the preceding claims wherein the resin cook antioxidant is a primary antioxidant, a secondary antioxidant or mixtures thereof.

10. A baked pigmented paint according to any one of the preceding claims wherein the resin cook antioxidant is a secondary antioxidant selected from the group consisting of triphenylphosphite and tri(substituted-phenyl)phosphites.

11. A high performance thermosetting polyester resin according to any one of claims 1 to 10 wherein the resin cook antioxidant is pentaerythrityl-tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate].

12. A pigmented paint composition suitable for coating onto steel and baking to provide a baked pigmented paint with an L value of less than 70 units when measured according to ASTM D2244 and having high outdoor weatherability, said paint including:

a pigment or pigment mixture selected to provide an L value of less than 70 after baking; and a high performance thermosetting resin present in an amount of 40-60% by weight of the pigmented paint composition.

13. A pigmented paint composition according to claim 12 wherein the pigment or pigment mixture is selected to provide an L value of less than 40 after baking.

14. A pigmented paint composition according to claim 12 or 13 wherein the high performance thermosetting resin is present in an amount of 45-55% of unbaked paint.

15. A pigmented paint composition according to claim 14 wherein the high performance thermosetting resin is present in an amount of 50% by weight of the pigmented paint composition.

16. A pigmented paint composition according to any one of claims 12 to 15 wherein the pigment or pigment mixture is present in an amount of 15-25% by weight of the pigmented paint composition.

17. A pigmented paint composition according to claim 16 wherein the pigment or pigment mixture present in an amount of 20% by weight of the pigmented paint composition.

18. A pigmented paint composition according to any one of claims 12 to 17 including a cross-linker present in an amount of 5-10% by weight of the pigmented paint composition.

19. A pigmented paint composition according to any one of claims 12 to 18 including a solvent in an amount of 10-40% by weight of the pigmented paint composition.

20. A pigmented paint composition according to any one of claims 12 to 19 further including one or more paint additives selected from the group consisting of catalysts desiccants, surfactants, antiblock agents, pH adjusters and thickeners.

21. A pigmented paint composition according to any one of claims 12 to 20 wherein the high performance resin is selected from the group consisting of fluorocarbons, polyesters, silicone polyesters, alkyds, acrylics, silicone acrylics, polyurethanes, polyester-urethanes, silicone alkyds and mixtures thereof.

22. A pigmented paint composition according to any one of claims 12 to 20 wherein the high performance resin is a polyester resin

23. A pigmented paint composition according to any one of claims 12 to 22 wherein the pigment or mixture of pigments includes one or more members selected from the group consisting of titanium dioxide, ultramarine blue, phthalocyanine blue, phthalocyanine green, carbon black, black iron oxide, chromium green oxide, ferrite yellow and quindo red.

24. A pigmented paint composition according to any one of claims 12 to 23 wherein the resin cook antioxidant is a primary antioxidant, a secondary antioxidant or mixtures thereof.

25. A pigmented paint composition according to any one of claims 12 to 24 wherein the resin cook antioxidant is present in an amount less than 5% by weight of the resin.

26. A pigmented paint composition according to any one of claims 12 to 24 wherein the resin cook antioxidant is a secondary antioxidant selected from the group consisting of triphenylphosphite and tri(substituted-phenyl)phosphites.

27. A pigmented paint composition according to any one of claims 12 to 24 wherein the resin cook antioxidant is pentaerythrityl-tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate].

28. A high performance thermosetting polyester resin incorporating a resin cook antioxidant and suitable for formulation into a baked pigmented paint with an L value of less than 70 units when measured according to ASTM D2244 and having high outdoor weatherability and suitable for use in coated steel products, said high performance polyester resin including:

an acid component set comprising diacids and/or triacids and/or monoacids and their anhydride analogues where applicable,
an alcohol component set comprising diols and/or triols and/or mono-alcohols; and
a resin cook antioxidant.

29. A high performance thermosetting polyester resin according to claim 28 wherein the acid component has 60-100 mole% of an aromatic acid, aromatic diacid, aromatic anhydride or mixtures thereof and 0-40 mole% of a non-aromatic acid, non-aromatic diacid, non-aromatic anhydride or mixtures thereof.

30. A high performance thermosetting polyester resin according to claim 29 wherein the acid component has 90-100 mole% of an aromatic acid, aromatic diacid, aromatic anhydride

or mixtures thereof and 0-10 mole% of a non-aromatic acid, non-aromatic diacid, non-aromatic anhydride or mixtures thereof.

31. A high performance thermosetting polyester resin according to any one of claims 28 to 30 wherein the total alcohol component has a trihydroxy compound in an amount of 5 to 20 mole%, neopentyl glycol in an amount of 0 to 60 mole% and 40-95 mole% of a glycol selected from the group consisting of 2-butyl-2-ethyl-1,3-propanediol; neopentylglycol hydroxypivalate and glycols having a carbon atom β to a hxydroxyl group mono- or di- substituted with a methyl, ethyl, propyl or butyl group(s).

32. A high performance thermosetting polyester resin according to any one of claims 28 to 31 having equimolar amounts of acid and hydroxyl groups, an acid value in the range of 0 to 100, a hydroxy value in the range 20 to 110 and a number average molecular weight in the range 700 to 50000.

33. A high performance thermosetting polyester resin according to any one of claims 28 to 32 having an acid value in the range 0 to 10.

34. A high performance thermosetting polyester resin according to any one of claims 28 to 33 having a number average molecular weight in the range 700 - 8000

35. A high performance thermosetting polyester resin according to any one of claims 28 to 34 wherein the trihydroxy compound is trimethylolethane or trimethylolpropane present in an amount of 10-20 mole% of the total alcohol component.

36. A high performance thermosetting polyester resin according to any one of claims 28 to 35 wherein the resin cook antioxidant is a primary antioxidant, a secondary antioxidant or mixtures thereof.

37. A high performance thermosetting polyester resin according to any one of claims 28 to 36 wherein the resin cook antioxidant is a secondary antioxidant selected from the group consisting of triphenylphosphite and tri(substituted-phenyl)phosphites.

38. A high performance thermosetting polyester resin according to any one of claims 28 to 37 wherein the resin cook antioxidant is present in an amount less than 5%

39. A high performance thermosetting polyester resin according to any one of claims 28 to 38 wherein the resin cook antioxidant is in an amount of 0.01 to 2.0% by weight of the total resin.

40. A high performance thermosetting polyester resin according to any one of claims 28 to 39 wherein the resin cook antioxidant is triphenylphosphite.

41. A high performance thermosetting polyester resin according to any one of claims 28 to 40 wherein the resin cook antioxidant is pentaerythrityl-tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionate].

42. A high performance thermosetting polyester resin according to any one of claims 28 to 41 wherein the resin cook antioxidant is present in an amount of 0.01 to 0.02% by weight of the total resin.

43. A high performance thermosetting polyester resin according to any one of claims 28 to 41 further including one or more of degassing agents, flow control agents and biocides.

Dated this 21st day of April 2005

BLUESCOPE STEEL LIMITED

FIGURE 1

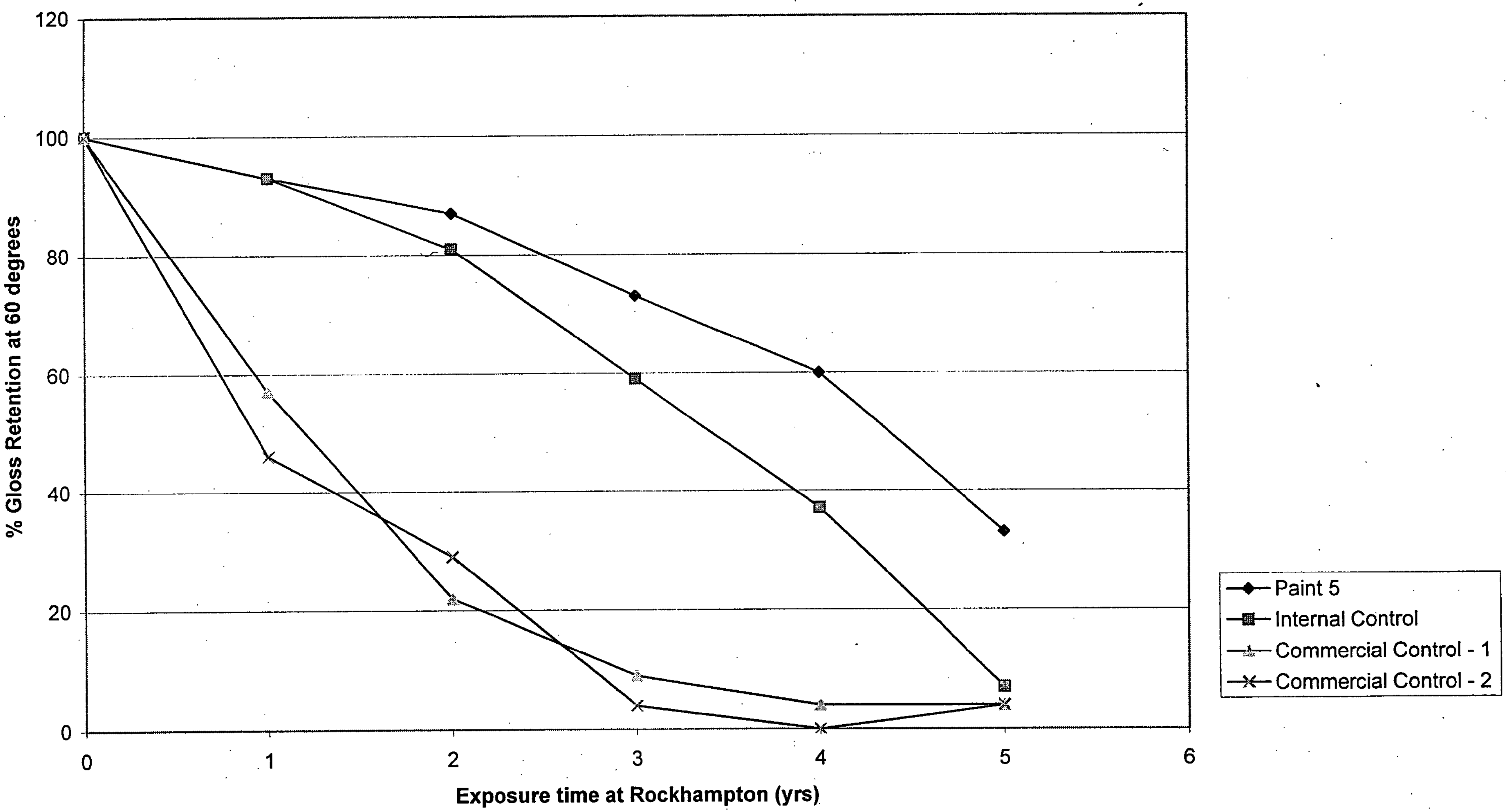
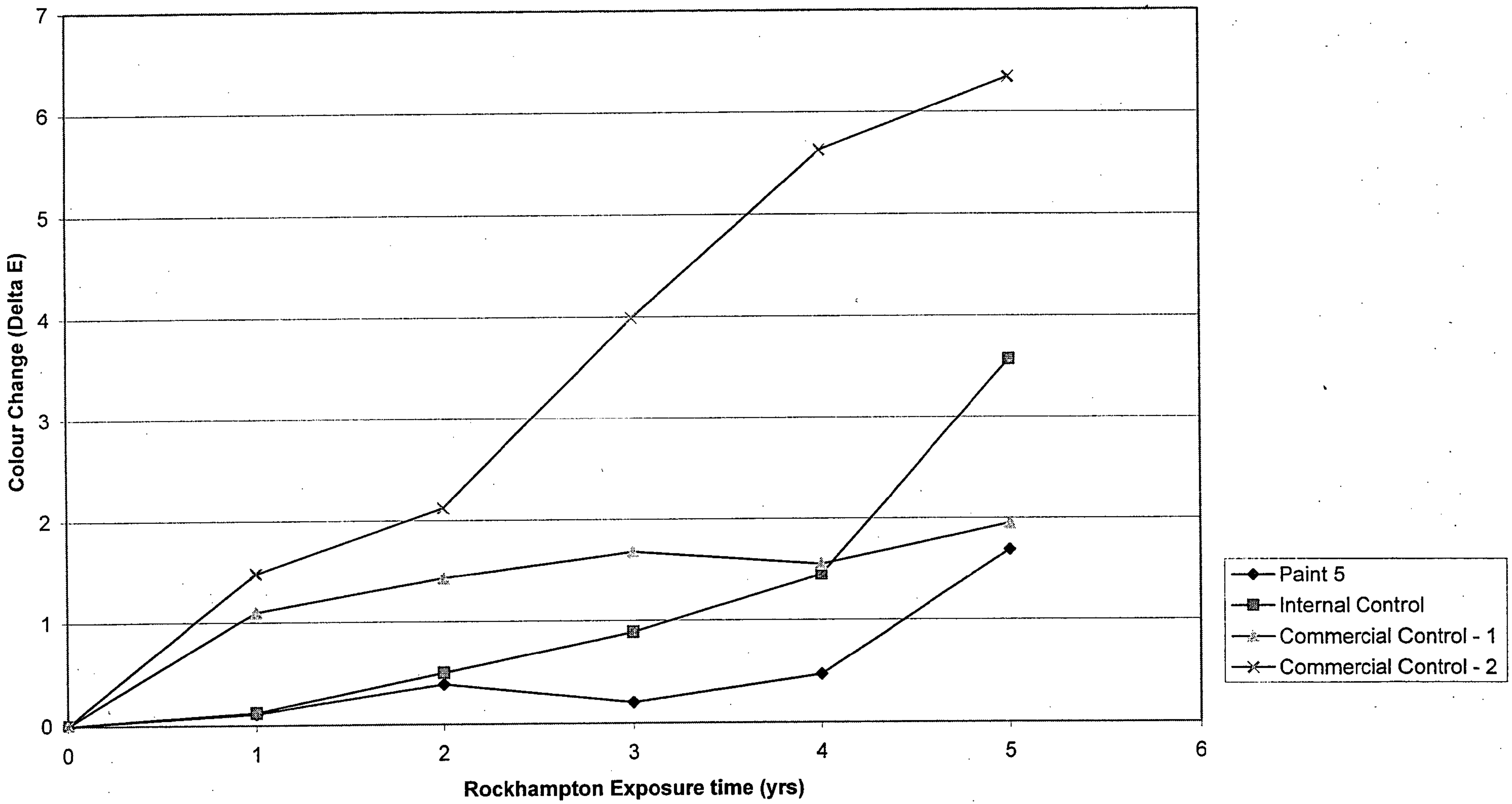

120
100
80
60
40
20
0
% Gloss Retention at 60 degrees
0
1
2
3
4
5
6
Exposure time at Rockhampton (yrs)
Paint 5
Internal Control
Commercial Control - 1
Commercial Control - 2

FIGURE 2 -


Colour Change (Delta E)
0
1
2
3
4
5
6
7
Rockhampton Exposure time (yrs)
0
1
2
3
4
5
6
Paint 5
Internal Control
Commercial Control - 1
Commercial Control - 2