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(71) **Applicant** *(for all designated States except US)*: **AKZO NOBEL POWDER COATINGS (NINGBO) CO. LTD.** [CN/CN]; Ningchuan Road, Wuxiang Town, Yinzhou District, Ningbo, Zhejiang 315111 (CN).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **ZHAO, Hui** [CN/CN]; c/o Akzo Nobel Powder Coatings (Ningbo) Co. Ltd., Ningchuan Road, Wuxiang Town,Yinzhou District, Ningbo, Zhejiang 315111 (CN). **WANG, Xiaodong** [CN/CN]; c/o Akzo Nobel Powder Coatings (Ningbo) Co. Ltd., Ningchuan Road, Wuxiang Town,Yinzhou District, Ningbo, Zhejiang 315111 (CN). **CHAKRAVORTY, Nirmalya** [IN/IN]; A-2, Acacia Primrose, 3rd Cross, Keerthy Layout, Bangalore, Kamanahalli, 560084 (IN).

(74) **Agent**: **ZHONGZI LAW OFFICE**; 7F, New Era Building, 26 Pinganli Xidajie, Xicheng District, Beijing 100034 (CN).

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(54) **Title**: POWDER COATING HAVING ANODIZED LOOK

(57) **Abstract**: A powder coating composition comprises the following ingredients: (a) a binder resin, (b) a solvent soluble dye, (c) a matting effect compound, and (d) less than 10 wt. % of a pigment or dye that is not soluble in a solvent, based on the total weight of powder coating composition. When cured, the powder coating composition has an anodized look. A substrate having an anodized look is also provided, which has an ADE-index above 3.

POWDER COATING HAVING AN ANODIZED LOOK

The present invention relates to a powder coating composition that will result, when cured, in a special effect coating, viz. a coating with an anodised look.

Powder coating compositions are solid compositions that generally comprise a solid film-forming resin, usually with one or more pigments and, optionally, one or more performance additives such as plasticizers, stabilizers, flow aids and extenders. The resins are usually thermosetting, incorporating, for example, a binder resin and a corresponding crosslinking agent (which may itself be another binder resin). Generally, the resins have a T_g, softening point or melting point above 30°C.

Conventionally, the manufacture of a powder coating comprises melt-mixing the components of the composition. Melt-mixing involves the high speed, high intensity mixing of dry ingredients and then the heating of the mixture to an elevated temperature - above the softening temperature of the resin but below the curing temperature - in a continuous compounder to form a molten mixture. The compounder preferably comprises a single or twin screw extruder as these serve to improve the dispersion of the other ingredients in the resin as the resin melts. The molten mixture is extruded, typically rolled in the form of a sheet, cooled to solidify the mixture and subsequently crushed (pulverized).
Such processing is then generally followed by a sequence of particle sizing and separation operations - such as grinding, classifying, sifting, screening, cyclone separation, sieving and filtering - that precede the application of the powder to a substrate and the heating of that powder to melt and fuse the particles and to cure the coating. The main methods by which powder coatings are applied include fluidized-bed and electrostatic fluidized- bed processes and electrostatic

spray processes in which the powder coating particles are electrostatically charged by a spray gun and directed onto an earthed substrate.

Anodising is an electrochemical process wherein a protective layer of aluminium oxide is formed on the surface of an aluminium sheet. This layer can be coloured by dyeing the electrochemical bath. Anodising gives aluminium a deeper, richer metallic appearance than possible with organic coatings. An anodised surface is translucent, so the base metal underneath stays visible, even after the treatment.

This anodised look is desired for various applications and various substrates, not only aluminium substrates.

An anodised look can be measured in an objective way by determining the reflection along and across the observed texture. For each measurement the L, a and b values can be recorded and the color differences along and across the texture can be calculated using the standard colour difference equation. When the reflection is measured at the flop angle (110° from the specular reflection) for a surface with an anodised look a ΔE(along – across texture) is larger than 3 is found. For non-anodised surfaces at low or high gloss a ΔE(along – across texture) smaller than 2 is found.

For the purpose of the present invention, a surface having an anodised look is a surface having a ADE-index larger than 3, where the ADE-index is defined as ΔE(along – across texture) measured in accordance with the method described above.

Currently, no coatings are available, both solvent based coatings and powder coatings, to produce a coating with an anodised look without the need to use the well-known electrochemical process.

In GB 1363741 various powder coating compositions are disclosed. These powder coating compositions when applied to a substrate and cured will not give an anodised look.

In US6800334 various powder coating compositions are disclosed. These powder coating compositions when applied to a substrate and cured will not give an anodised look.

In EP 1347021 various powder coating compositions are disclosed. These powder coating compositions when applied to a substrate and cured will not give an anodised look.

In JP 63243176 various powder coating compositions are disclosed. These powder coating compositions when applied to a substrate and cured will not give an anodised look.

In WO 2007/060070 various powder coating compositions are disclosed. These powder coating compositions when applied to a substrate and cured will not give an anodised look.

In JP 2006185525 various powder coating compositions are disclosed. These powder coating compositions when applied to a substrate and cured will not give an anodised look.

It was found that substrates with an anodised look can be obtained when a powder coating is applied and cured than contains transparent pigments and that is substantially free of any non-transparent pigments. None of the documents mentioned above discloses such combination and also no teaching or suggestion is present that this combination could result in powder coatings that can be used to generate such anodised look on a substrate.

Therefore, the current invention relates to a powder coating composition is used comprising

a. a binder resin,
b. a solvent soluble dye,
c. a matting effect compound, and
d. less than 10 wt.% of a pigment or dye that is not-soluble in a solvent, the wt.% based on the total weight of the powder coating composition.

In one embodiment of the invention the solvent soluble dye is a metal complex dye.

In a further embodiment of the invention the powder coating composition comprises an agent that enhances the solubility of the dye in the binder resin.

In a further embodiment of the invention the agent that enhances the solubility of the dye in the binder resin comprises isocyanates groups.

In a further embodiment of the invention the agent that enhances the solubility of the dye in the binder resin comprises caprolactam blocking groups.

Another embodiment of the invention relates to a process for the manufacture of a substrate with an anodized look wherein a powder coating composition comprising

a. a binder resin,

b. a solvent soluble dye,
c. a matting effect compound, and
d. less than 10 wt.% of a pigment or dye that is not-soluble in a solvent, the wt.% based on the total weight of the powder coating composition

is applied to the substrate, the substrate is heated, and the powder coating is cured.

The resins and the crosslinking systems in the powder composition are not intended to be limiting features of the present invention. Accordingly, suitable resins for inclusion within the powder coating premix include both thermoplastic and thermosetting base resins.

When used in powder coatings, thermoplastic resins must melt and flow out to a thin film within a few minutes at stoving temperatures from 120°C to 300°C without significant degradation. As a result, suitable thermoplastic resins for use in the practice of the present invention include polyamides, polyesters, cellulose esters, polyethylene, polypropylene, poly(vinyl chloride) [PVC], poly(vinylidene fluoride) [PVF2], polyphenylsulfones and poly(tetrafluoroethylene) [PTFE] of which polyphenylsulfones and PTFE are particularly preferred. All of the suitable thermoplastic resins are readily available from commercial sources.

The thermosettable resins which are suitable for this invention include epoxy resins, polyurethanes, silicones, crystalline resins, polyesters (including unsaturated polyesters), acrylics, and hybrids such as epoxy-acrylic, polyester-acrylic, and epoxy-polyester. The glass transition temperature (T_g) of these resins must be high enough that the particles do not fuse together or sinter at temperatures likely to be encountered during transportation and storage.

Preferably, the T_g is in the range from 45° to 120°C, within which range a T_g greater than 55° is more preferred.

EPOXY RESINS

Suitable epoxy resins are those containing aliphatic or aromatic backbones with oxirane functionality and are exemplified by: the diglycidyl ether condensation polymers resulting from the reaction of epichlorohydrin with a bisphenol e.g. bisphenol A and bisphenol F in the presence of an alkaline catalyst; and, glycidyl ethers of phenolic novolac resins synthesised by reacting phenolic novolac resin with epichlorohydrin in presence of sodium hydroxide as a catalyst.

Generally the epoxy resins should have: an epoxide equivalent weight (EEW) between 600 and 2000; a hydroxyl equivalent weight between 300 and 400; and, a melt viscosity in the range from 200 to 2000 centipoise (cps) at 150°C, preferably from 300 to 1000 cps. The low melt viscosities of such resins may allow them to be extruded at temperatures less than 200°C.

Commercially available epoxy resins which are preferred for the purposes of this invention are the bisphenol A epoxies sold under the trademarks ARALDITE® GT-7004, GT-7071, GT-7072, GT-6259 (Huntsman LLC) EPON® 1001 and 2042 (Shell Chemicals, Inc.).

A wide variety of curing agent for epoxy resins is available depending on the process and properties required. Dicyandiamide, modified and substituted dicyandiamides, solid dicarboxylic acids and their anhydrides are examples of those agents that may be used for the curing of epoxy resins. A curing agent in solid form is preferred for convenience in the formulation of epoxy resin-based powders as well as in the formulation of other resin-based powders in this invention.

SILICONE RESINS

Silicone resins for use in this invention should be: solid at room temperature; have a T_g of greater than 55° C, preferably greater than 60°C; and a viscosity of between about 500 and about 10,000 cps at 150° C, preferably 2000 to 5000 cps.

Suitable silicone resins for use in this invention are described *inter alia* in U.S. Patents Nos. 3,170,890; 4,879,344; 3,585,065; and, 4,107,148 the disclosures of which are herein incorporated by reference. Examples of suitable, commercially available silicone resins are phenylsilicone SY-430 and methylsilicone MK (both products of Wacker Silicone, USA) and methylphenylsilicone 6-2230 (Dow Corning).

HYDROXY-FUNCTIONAL POLYESTER RESINS

Suitable hydroxy functional polyesters for use in the process of this invention are predominantly hydroxyl in functionality and should preferably be characterized by having: i) a hydroxyl number in the range from about 25 to about 50; ii) an acid number less than or equal to 15 but preferably in the range from about 1 to 2; and, iii) a T_g higher than 50°C.

Hydroxy functional polyesters meeting these requirements are commercially available as RUCOTE ® 107, CARGILL ® 3000 / 3016, and CRYLCOAT ®

3109. Equally, however such polyesters may be formed as the condensation products of polybasic carboxylic acids and polyhydric alcohols. As such, carboxylic acids useful for the preparation of such polyester resins include one or more of phthalic acid, tetra- and hexahydrophthalic acids and their anhydrides, succinic acid, adipic acid, sebacic acid, terephthalic and isophthalic acids, 1,3- and 1,4-cyclohexane-dicarboxylic acids, and trimellitic anhydride, esters of such acids. Further, suitable difunctional alcohols include ethylene-, diethylene-, propylene-, isomers of 1,2 and 1,3 propylene glycol and trimethylene glycol and suitable dihydric alcohols include hexanediol, 1,3-, 1,2-, and 1,4-butanediols, neopentyl glycol, 2-butyl-2-ethyl-1,3-propanediol, 2-methyl-1,3-propanediol, 1,4-cyclohexanediol, trimethylolpropane, and mixtures thereof. The skilled reader will be aware of a number of such acids and alcohols and processes for carrying out the condensation of the acids and alcohols.

The hydroxyl-functional polyesters are curable through the hydroxyl groups with aliphatic and aromatic isocyanates and with aminoplasts. Isocyanate curing forms resins which technically are polyesters but when cured are described as polyurethanes. Aminoplasts are oligomers that are the reaction products of aldehydes, particularly formaldehyde, with amino- or amino-group-carrying substances exemplified by melamine, urea, dicyandiamide, and benzoguanamine. It is preferable in many instances to employ precursors of aminoplasts such as hexamethylol melamine, dimethylol urea, and their etherified forms, i.e., modified with alkanols having from one to four carbon atoms. Hexamethoxymethyl melamine and tetramethoxy glycoluril exemplify said etherified forms. Particularly preferred are the amino cross-linking agents CYMEL ® available from American Cyanamid. Thus, a wide variety of commercially available aminoplasts and their precursors can be used for combining with hydroxyl functional polyesters of this invention.

Aminoplast curing agents are typically provided in an amount sufficient to react with at least one-half the hydroxyl groups of the polyester, i.e., an amount at least one-half the stoichiometric equivalent of the hydroxyl functionality. Those skilled in the art will choose the correct stoichiometric ratio and catalyst level to achieve the desired coating performance. Preferably, the amount of cross-linking agent is sufficient to substantially completely react with all of the hydroxyl functionality of the polyester, and cross-linking agents having nitrogen cross-linking functionality are provided in amounts of from about 2 to about 12 equivalents of nitrogen cross-linking functionality per equivalent of hydroxyl functionality of the polyester.

Acidic catalysts may be used to modify the curing of the polyester with an aminoplast resin by lowering the required temperature or raising the reaction rate or both. When it is desirable to lower the rate at ambient storage temperatures, the acidic catalyst may be blocked with an amine. Volatile amines which may escape from the curing film when the catalyst is unblocked by heat are suitable for this purpose. It is particularly desirable for the purposes of this invention to delay full curing of the composition. NACURE ® 1557, an amine-blocked dinonylnaphthalenesulfonic acid available King Industries, is an example of the blocked acid catalyst suitable for use in the aminoplast curing of the powder coating composition of this invention.

Diisocyanates cure hydroxy-functional polyester resins by forming urethane linkages between the polymer chains at the hydroxyl group sites. Common aliphatic diisocyanates are exemplified by hexamethylene diisocyanate (HDI), diisocyanato di-cyclohexylmethane (sold as DESMODUR W® by MIles Chemical) and isophorone diisocyanate (IPDI). Toluene diisocyanate (TDI) is an example of a suitable aromatic diisocyanate. The low-temperature reactivity of free diisocyanates may be reduced by adducting them with blocking agents selected from phenol, cresols, isononylphenol, amides such as epsilon - caprolactam, oximes such as methyl-ethyl ketoxime and butanoneoxime, active methylene group-containing compounds such as diethylmalonate, and isopropylidene malonate and the acetoacetates, and sodium bisulfite. Examples of the blocked diisocyanates include caprolactam blocked isophorone diisocyanate and caprolactam blocked hexamethylene diisocyanate. Examples of commercially available curing agents of this type are the 24-2400, 24-2430, and 24-2450 products sold under the CARGILL trademark. Another group of blocked curing agents are the uretdiones which can be described as internally blocked.

CARBOXY FUNCTIONAL POLYESTER RESINS

Carboxyl-functional polyesters are also suitable for the purposes of this invention. These may be made from the same polyfunctional acids and glycols as the hydroxyl-functional polyesters but with an excess of the acids. The acid number is from about 10 to about 100. Suitable commercial products are: CRYLCOAT ® 430, 3010 and 7617 (available from UCB); URALAC ® 3400 and 3900; EL6500 or EL6700 or EL8800 available from Chan Sieh Enterprises Fast cure of these carboxy functional polyesters may be achieved with polyepoxide curing agents such as triglycidyl isocyanurate (TGIC).

Further alternatives curing agents to TGIC include: Primids, such as Primid XL552 and QM1260 which are hydroxyalkylamides available from EMS-Primid; Araldite PT910 gylcidyl ester available from Ciba Geigy; and Uranox available from DSM.

Unsaturated polyesters suitable for use in the practice of the invention include ethylenically unsaturated reaction products of an organic di- or polyfunctional acid and a di- or polyfunctional alcohol. Typically the acid is unsaturated. Such polyester resins typically work best in combination with a copolymerizable second resin such as diallyl phthalate. Initiators may also need to be incorporated.

ACRYLIC RESINS

The preferred acrylic resins for powder coatings are copolymers of alkyl acrylates and/or methacrylates with glycidyl-methacrylates and/or acrylates and olefinic monomers such as styrene. Glycidyl-functional acrylic resins are sold by Mitsui Toatsu Chemicals, Inc. as ALMATEX ® for which a carboxy-terminated polymer may be used as a cross-linking agent. Hydroxyalkyl acrylate and methacrylate copolymers are also suitable for this invention.

HYBRID RESIN SYSTEMS

Hybrid resin systems, such as the epoxy-acrylic and polyester-acrylic mixtures, are also suitable for this invention. However, where such a system is employed, it is preferably a polyester-epoxy hybrid. As known in the art, polyester-epoxy hybrids comprise both epoxy resins and carboxyl terminated polyester resins and may also comprise a catalyst to drive the curing reaction. Typically, the acidic polyester has an equivalent weight between 600 and 4000 and the epoxy resin has an equivalent weight between 400 and 1100. Catalysts for the epoxy-acid reaction include quaternary ammonium salts, quaternary phosphonium salts, phosphines, amines, imidazoles and metal salts. Amphoteric catalysts such as, zinc oxide (ZnO_2) is effective at 1-5 parts per hundred parts by weight of the resins to improve the cure rate and physical properties of the product.

The powder coating composition according to the present invention also comprises a solvent soluble dye. Such dyes normally show good solubility in solvents like alcohol, ketones, and glycol ether and ester solvents.

In one embodiment of the invention the solvent soluble dye is a metal complex dye. Metal-complex dyes are also known as pre-metallized dyes. Metal complex dyes find application for dyeing fibres, both natural and synthetic fibres such as polyamide fibres and wool. Chemically speaking, Metal complex Dyes can be broadly classified into two classes. 1:1 metal-complexes, where, one dye molecule gets co-ordinated with a single metal atom. In 1:2 metal complexes, one metal atom is co-ordinated with double dye molecules. The dye molecules are typically a monoazo structure which can contain additional groups like hydroxyl, carboxyl or amino groups. They can form strong co-ordination complexes with transition metal ions, like Nickel, Chromium, Cobalt and Copper..

In one embodiment of the invention the solvent soluble dye is 1:2 metal complex dye.

Examples of solvent soluble dyes that can be used in the coating compositions according to the present invention include metal complex dyes, fluorescent dyes, polymer soluble dyes, and polysynthren dyes. An example of a dyes that can be used in the coating compositions of the present invention are Savinyl ® - type dyes supplied by Clariant

It was found that such dyes show a good solubility in the binder resin, in particular when a polyester binder resin is used.

When a resin or a mixure of resins is used with mediocre or poor solubility of the dye, it was found that the solubility can be enhanced by using a compound that has isocyanates groups. In another embodiment it was found that the solubility can be enhanced by using a compound with caprolactam groups. It is also possible to use a compound that has both isocyanates functionality and caprolactam functionality, for example a compound having isocyanates groups blocked with ε-caprolactam. Examples of a compounds that can be used to improve the solubility of the dye in the binder resin include Vestagon® B1530 (an ε-caprolactam blocked polyisocyanate ex. Degussa) and Vestagon ® B1540 (a blocked uretdione compound, ex Degussa_.

The coating composition according to the present invention also comprising a matting effect compound. In combination with a soluble dye, a matting effect compound is an essential ingredient to get a cured powder coating with an anodised look.

Within the framework of the present application, a matting effect compound is a compound that is added to the composition to get a matting effect. In the composition according to the present invention various types of matting effect compounds can be used, such as:

- a wax, or a mixture of waxes;
- a second binder resin with a gel time that is different from the gel time of the binder resin that is already present in the composition;
- a gloss reducing agent that reacts with the binder resin;
- a hardener with different reactive groups, where the reactive groups show a different reactivity towards the binder resin;
- a high amount of a filler with coarse particles.

Suitable waxes can be selected from the group consisting of polyamide wax and polyethylene wax. The waxes can have modifications, such as being micronised or PTFE-modified. In general, the waxes have a melting temperature in the range of 100 to 160 °C.

An example of the use of a second binder resin can be found in compositions comprising two different types of polyester resins, one type of polyester resin with a relatively short gel time, the other type of polyester resin with a relatively long gel time.

An example of a gloss reducing agent that reacts with the binder resin is Synthacryl 700, when used in combination with a polyester binder resin. Another example of such compound is T-325, a resin based delustering agent, when used in a polyester/epoxy hybrid binder system.

An example of a hardener with different reactive groups is Vestagon B68, when used in combination with an epoxy resin.

Barium sulphate and calcium carbonate with coarse particles can be used in relatively high amounts to obtain a cured powder coating with a matt appearance.

In addition to the resin systems, the dye, and the matting effect compounds described above the powder coating compositions may comprise other components that are conventionally known in the art. These may include: fillers, flow control agents, degassing agents, and antiblocking agents.

The powder coating composition according to the present invention contains less than 10 wt.% of a pigment or dye that is not-soluble in a solvent, the wt.% based on the total weight of the powder coating composition.

In one embodiment, the powder coating composition according to the present invention is substantially free of any non-transparent pigments, but it can contain small amounts of transparent pigments. High amounts of pigments may destroy the anodised/translucent look of the coating. In the context of the present invention, substantially free means that the composition contains less than 0,5 wt.% of any non-transparent pigment, more in particular less than 0,1 wt.% of any non-transparent pigment. In one embodiment, the composition does not contain any non-transparent pigments, but it can contain small amounts of transparent pigments.

Examples of non-transparent pigments include inorganic pigments such as titanium dioxide, red and yellow iron oxides, chrome pigments and carbon black.

Further suitable additives for the powder coating composition may include: adhesion promoters; light stabilizers and UV absorbers; flow and leveling additives; gloss-modifying additives; cratering agents; cure agents; texturizers; surfactants; wetting agents; antioxidants (in particular phosphites, hindered phenols and propionates); biocides; and, organic plasticizers.

Fillers may be employed to reduce cost and/or reinforce or modify the performance and appearance of the coatings. Fillers comprising glass particles, glass fibres, metal fibers, metal flakes and particles of micas or calcium metasilicate could be included in the powder coating compositions of this invention. Inorganic sulphates such as barites, carbonates such as chalk, and silicates such as talc are commonly used.

Metallics including zinc rich anticorrosive particulates may be added to powder coating compositions to impart corrosion resistance to the underlying substrate.

Flow control agents may be present in the powder coating compositions in an amount up to 3 wt. % based on the weight of the composition. Such flow control agents, which enhance the compositions melt-flow properties and assist in eliminating surface defects, typically include acrylics and fluorine based polymers. Examples of commercially available flow control agents include: Resiflow® P-67, Resiflow® P-200 and Clearflow® (all available from Estron Chemical Inc., Calvert City, KY); BYK® 361 and BYK® 300 from BYK Chemie (Wallingford, CONN); Mondaflow® 2000 from Monsanto (St. Louis, MO); and, Acranal 4F from BASF.

Degassing agents can also be used in the powder coating compositions of the present invention in an amount between 0.1 and 5 wt. %, based on the weight of the composition. Such degassing agents facilitate the release of gases during the curing process. Examples of commercially available degassing agents include: Benzoin available from Well Worth Medicines; and, Uraflow® B available from GCA Chemical Corporation (Brandenton, FLA).

The powder coating compositions may also comprise an antiblocking agent (dry-flow additive) in an amount from 0.05 to 1.0 wt. %, based on the total weight of the composition. Examples of such additives include fumed silica, precipitated silica, fumed alumina, clay, talc and mixtures thereof.

A typical powder coating compositions according to the present invention can have the following ingredients:

40 – 95	wt.% of a binder resin or a mixture of binder resins;
0,2 – 2	wt.% of a solvent soluble dye
0,2 – 60	wt.% of a matting effect compound
0 – 8	wt.% of a curing agent;
0 – 25	wt.% of an agent to enhance the solubility of the dye
0,2 – 5	wt.% of other ingredients

the above wt.% being calculated on basis of the total weight of the powder coating composition and the sum of all ingredients in the powder coating composition adding up to 100 wt.%.

A typical powder coating compositions according to the present invention based on a polyester binder resin can have the following ingredients:

40 – 60	wt.% of a first polyester resin;
40 – 60	wt.% of a second polyester resin, having a different gel time than the first polyester resin, acting as a matting effect compound;
2 – 8	wt.% of a curing agent;
0,2 – 2	wt.% of a solvent soluble dye
0,2 – 5	wt.% of other ingredients

the above wt.% being calculated on basis of the total weight of the powder coating composition and the sum of all ingredients in the powder coating composition adding up to 100 wt.%.

A typical powder coating compositions according to the present invention based on a hybrid binder resin can have the following ingredients:

30 – 50	wt.% of a polyester resin;
30 – 50	wt.% of an epoxy resin;
0,2 – 2	wt.% of a solvent soluble dye
0,2 – 5	wt.% of a matting effect compound
0 – 8	wt.% of a curing agent;
0 – 25	wt.% of an agent to enhance the solubility of the dye
0,2 – 5	wt.% of other ingredients

the above wt.% being calculated on basis of the total weight of the powder coating composition and the sum of all ingredients in the powder coating composition adding up to 100 wt.%.

The powder coating according to the present invention can be applied over a wide range of applied film thicknesses, typically from thin films of, for example, 30 microns or less up to films of 50, 100, 150 or 200 microns. A typical minimum film thickness is 5 microns.

The powder coating according to the present invention can be applied by electrostatic spray equipment. Normally, the powder is sprayed under 60 – 80 KV at a film thickness between 40 – 60 micron. Unused powder can be collected and recycled through the application system.

The powder coating composition according to the present invention can be applied to a wide range of substrates, such a metal, wood, and plastic. The best results on substrates having an anodised look were found when the powder coating compositions are applied to an aluminium substrate.

ADE-INDEX

The ADE-index is an objective way to quantitatively describe a genuine anodised surface or a surface with an anodised look. The ADE-index can be measured using apparatus that are able to do color measuring at discrete angles in a plane.

For this measurement, for example, an X-rite MA68II portable multi angle spectrophotometer can be used.

The ADE-index can be measured by determining the reflection along and across the observed texture. For each measurement the L, a and b values are recorded and the color differences along and across the texture are calculated using the standard colour difference equation. The reflection is measured at the flop angle (110° from the specular reflection) of the surface to be measured. The ADE-index is ΔE(along – across texture). For a surface having of a genuine anodised object or of an object with an anodised look an ADE-index of larger than 3 is found. For non-anodised surfaces or surfaces not having an anodised look at low or high gloss an ADE-index smaller than 2 is found.

In another embodiment, the invention relates to a substrate coated with a powder coating having an anodised look, which means that the coated surface has an ADE-index of larger than 3.

The powder coatings according to the present invention show a number of advantageous properties when subjected to various mechanical or chemical tests known to the skilled person. The properties have been listed in the table below:

Type of test	Test procedure	Test result
Norman abrasion	ASTM F2357-04	No visual wear through to substrate or other paint layer after 150 cycles
Taber abrasion	ASTM D4060-07	<100 mg loss of coating weight
Adhesion	ASTM D3359 -09	5B with 1mm squares
Pencil Hardness	ASTM D3363-05	F~H, no scratches visible under 5x magnification
Direct Impact	ASTM D2794-93	No visible damage to film up to 20 kg.cm with 16 mm ball diameter
Mandrel Bend	ASTM D522 – 93a	No visible damage to film with ¼” mandrel
Chemical Sensitivity	ASTM D1308-02	No visible stain with common cosmetics and/or cleaners
Water resistance in 100% RH	ASTM D2247 – 02	No visible change after 500 hours
Practical Washability	ASTM D4828 – 94	No visible change after 100 cycles (with DI water, 2.5% ethanol or 1.84% sodium hypochlorite
Solvent Resistance	ASTM D4752 – 03	No visible change after 20 double rubs with methyl ethyl ketone

All percentages given in the following examples are percentages by weight, based on the weight of the total composition, unless expressly stated otherwise.

Examples

In the examples described below the following ingredients are used:

Ingredient	**Description**
Curing agent 1	β-Hydroxyalkylamide, ex YaoHe for primid curing
Dye solubility enhancement agent	ε-Caprolactam blocked Polyisocyanate, ex Evonik
Degassing agent	Benzoin for degassing, ex Daming
Epoxy resin	Bisphenol A Epoxy resin, ex Nanya
Other ingredients	Includes: Hindered amine light stabilisers (HALS) Fillers Flowing agents
Matting effect compound 1	Saturated carboxylated polyester resin
Matting effect compound 2	T-325 ex Suoshi
Polyester resins 1	Saturated carboxylated polyester resin
Polyester resins 2	Saturated carboxylated polyester resin, ex Shenjian
Savinyl dyes	Metal complex dyes tuff, ex Clariant

Examples 1-6

The following polyester resin powder coating compositions were prepared

Example **Ingredient**	1	2	3	4	5	6
Polyester resins 1	47	47	47	47	47	47
Matting effect compound 1	45	45	45	45	45	45
Curing agent 1	5	5	5	5	5	5
Degassing agent	0.3	0.3	0.3	0.3	0.3	0.3
Savinyl Red 3GLS	0.5					
Savinyl Pink 6BLS		0.5				
Savinyl Orange RLSp			0.5			
Savinyl Blue GLS				0.5		
Savinyl Blue RS					0.5	
Savinyl Green 2GLS						0.5
Other ingredients	2.2	2.2	2.2	2.2	2.2	2.2

These compositions were sprayed on aluminium panels and cured for 10 - 15 minutes at 200°C. After curing all panels showed a brightly colored anodised look. When measured in accordance with the method described above, all coated panels showed an ADE-index of larger than 3.

Examples 7 – 12 hybrid systems

The following polyester/epoxy hybrid compositions were prepared:

Example **Ingredient**	7	8	9	10	11	12
Polyester resins 2	36	46	46	46	46	46
Epoxy resin	36	46	46	46	46	46
Matting effect compound 2	5	5	5	5	5	5

Degassing agent	0.3	0.3	0.3	0.3	0.3	0.3
Savinyl Red 3GLS	0.5					
Savinyl Pink 6BLS		0.5				
Savinyl Orange RLSp			0.5			
Savinyl Blue GLS				0.5		
Savinyl Blue RS					0.5	
Savinyl Green 2GLS						0.5
Dye solubility enhancement agent	20					
Other ingredients	2.2	2.2	2.2	2.2	2.2	2.2

These compositions were sprayed on aluminium panels and cured for 10 - 15 minutes at 200°C. After curing all panels showed a brightly colored anodised look. When measured in accordance with the method described above, all coated panels showed an ADE-index of larger than 3.

Claims

1. A powder coating composition comprising
    a. a binder resin,
    b. a solvent soluble dye,
    c. a matting effect compound, and
    d. less than 10 wt.% of a pigment or dye that is not-soluble in a solvent, the wt.% based on the total weight of the powder coating composition.

2. The powder coating composition of claim 1 wherein the solvent soluble dye is a metal complex dye.

3. The powder coating composition of claim 1 or 2 comprising an agent that enhances the solubility of the dye in the binder resin.

4. The powder coating composition of claim 3 wherein the agent that enhances the solubility of the dye in the binder resin comprises isocyanates groups.

5. The powder coating composition of claim 3 or 4 wherein the agent that enhances the solubility of the dye in the binder resin comprises caprolactam blocking groups.

6. The powder coating composition of claim 1, characterised in that the composition is substantially free of any non-transparent pigment.

7. A powder coating composition comprising

40 – 95	wt.% of a binder resin or a mixture of binder resins;
0,2 – 2	wt.% of a solvent soluble dye
0,2 – 60	wt.% of a matting effect compound
0 – 8	wt.% of a curing agent;
0 – 25	wt.% of an agent to enhance the solubility of the dye
0,2 – 5	wt.% of other ingredients,

which is substantially free of any non-transparent pigment,

the above wt.% being calculated on basis of the total weight of the powder coating composition and the sum of all ingredients in the powder coating composition adding up to 100 wt.%.

8. A process for the manufacture of a substrate with an anodized look wherein a powder coating composition according to any of claims 1 – 7 is applied to the substrate, the substrate is heated, and the powder coating is cured.

9. A substrate having an anodised look when coated with a powder coating composition according to any of claims 1 – 7.

10. The substrate of claim 9, characterised in that the substrate is an aluminium substrate.

11. A substrate coated with a powder coating, the coated surface having an ADE-index larger than 3.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2011/071629

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT,CNKI,WPI,EPODOC, powder? coating, powder? paint, resin, dye, solvent dye, metal complex dye, polymer soluble dye, fluorescent dye, matting, degloss+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN1445313A(SPREYRET CO. LTD.), 01 Oct. 2003 (01.10.2003) Claims 1 and 14, page 3 lines 17-19, page 8 line 1 to page 9 line 19, page 10 lines 8-30, page 15 lines 5-29 and table on page 12 of description	1-11
A	CN1524112A(CLARIANT FINANCE BVI LTD.), 25 Aug. 2004 (25.08.2004) the whole document	1-11
A	CN101161744A (JIANGMEN KEHENG INDUSTRY CO. LTD.), 16 Apr. 2008 (16.04.2008) the whole document	1-11
A	WO2007134736A2 (BASF COATINGS AG et al.),29 Nov. 2007 (29.11.2007) the whole document	1-11
A	CN1620482A(CLARIANT FINANCE BVI LTD.),25 May 2005(25.05.2005), the whole document	1-11

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"document member of the same patent family

Date of the actual completion of the international search 06.05.2011 (06.05.2011)	Date of mailing of the international search report **30 Jun. 2011 (30.06.2011)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer GAO Beibei Telephone No. (86-10)62084928

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2011/071629

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2011/071629

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2011/071629

A. CLASSIFICATION OF SUBJECT MATTER

C09D5/03(2006.01)i

C09D7/12(2006.01)i