(54) Title: POLYAMIDE-TYPE FLAME-RETARDANT COMPOSITION FOR POWDER COATING

(57) Abstract: Problems: To provide a polyamide-type flame-retardant composition for powder coating showing little discoloration and uniform performance without spoiling surface property, appearance and adhesion to substrate. Solution: Polyamide-type flame-retardant composition for powder coating consisting mainly of polyamide, characterized in that polyphosphoric acid type compound (excluding melamine phosphate) is incorporated as flame retardant.
POLYAMIDE-TYPE FLAME-RETARDANT COMPOSITION FOR POWDER COATING

Technical Field of Invention

This invention relates to a polyamide-type flame-retardant composition for powder coating, containing no halogen system flame retardant and possessing improved uniform fire retardant property with reduced discoloration in appearance.

Prior Arts

Surface coating is well-known and has been used since old days to protect metallic materials from rust and to improve appearance and properties of various materials. Organic coating materials such as ester type, epoxy type and combination thereof, urethane type, acryl type, polyamide type and fluorine type resins are used widely. These organic coating materials are usually dissolved or dispersed in organic solvent to facilitate handling and processing. Use of organic solvent, however, is not desirable from the view point of contamination in surrounding and in working environment and hence is controlled by laws. To solve this problem, water-soluble paints, water-dispersion paints and powder paint are developed as solvent-free paints and are used in practical uses.

A variety of additional functions or properties are required in coated products in each application, such as improvement in heat-resistance, weather-resistance and surface hardness.

In this invention, flame-retardant of polyamide film is improved.

Polyamide 6 and 66 which are used widely as molding material possess self-fire extinguish property because its oxygen index is 27. However, the oxygen indexes of polyamide 11 and 12 which are used in
powder coating are 22 to 25, so that its flame-proofing is difficult.

Several flame retardants of the inorganic and organic compounds are known. Generally, a combination of bromine compound and antimony compound is used since this combination is effective in smaller proportion. However, de-halogenation is now required from the view point of environment and health problems.

As non-halogen type flame-retardants, a variety of compounds such as metal hydroxides such as magnesium hydroxide, aluminum hydroxide, phosphor type compounds, guanidine type compounds, guanyl type compounds, urea type compounds and melamine type compounds are known. These non-halogen type flame-retardants, however, are used mainly in molding materials but are not applied to materials for powder coating.

Use of these compounds in powder coating materials are not so easy. In fact, when hydroxide is used in polyamide, there are many problems to be solved such as the effect of moisture in addition to affinity. In particular, it is a big problem how to disperse flame retardant uniformly, because a film produced by the powder coating technique is thin. Still more, adhesion to a substrate and surface condition are also important.

It is known to incorporate phosphorus compound in thermoplastic resins. For example, JP-A1-62-263247 discloses a effectiveness of red phosphorus. However, red phosphorus cannot be used in powder coating material in which color tone is important because of discoloration.

It is also known to add melamine phosphate to polyamide (for example, JP-A1-62- 62854). Actual use of melamine phosphate, however, is limited to films of dark color or low gloss because addition of melamine phosphate result in discoloration of film.
Problems to be solved by the Invention

An object of this invention is to obtain a flame-retardant film obtained by powder coating, possessing no discoloration, improved surface appearance and adhesion to a substrate.

Means to solved by the problems

This invention provides a polyamide-type flame-retardant composition for powder coating consisting mainly of polyamide, characterized in that polyphosphoric acid type compound (excluding melamine phosphate) is incorporated as flame retardant.

Embodiment of the Invention

Term "polyamide" is understood as polymers obtained from amino carboxylic acid having a carbon number of 6 or more than 6 or lactam, or salts of dicarboxylic acid and diamine having a carbon number of 6 or more than 6, and include, for example, amino carboxylic acid such as \(-\)amino caproic acid, \(-\)amino enanthic acid, \(-\)amino caprylic acid, \(-\)amino pelargonic acid, \(-\)amino capric acid, 11-amino undecane acid and 12-amino dodecane acid; lactam salt such as caprolactam, enanto lactam, capril lactam and laurolactam; salts such as salts of hexamethylenediamine-adipic acid, hexamethylenediamine-sebacic acid, hexamethylenediamine-isophthalic acid, undecamethylenediamine-adipic acid and 4,4\'-diaminocyclohexylmethane-dodecane diacid.

Polyamide can be homo polymer or copolymer and/or can be blended with other resin. Polyamide can contain also catalyst and various additives such as stabilizer. Polyamide 11 and 12 are preferably used.

Term "composition for powder coating" is understood as those obtained by powder-mixing the "polyamide" with a variety of additives
such as pigment, dye, heat-stabilizer, light-stabilizer, lubricant, plasticizer, antistatic agent and crystal nuclei agent, or those obtained by kneading components and then pulverized to obtain a powder for powder coating. If necessary, solid phase polymerization can be followed.

Powder coating can be done by any known technique including fluidized bed coating, electrostatic spray coating and molten spray coating.

The "flame retardant" used in the present invention is a compound selected from polyphosphoric acid type compounds such as salts and esters of polyphosphoric acid but melamine polyphosphate is excluded. Ammonium polyphosphate is preferable.

The particle size of the flame retardant in this invention is not limited specially but is preferably in a range of 1 to 200μm. In fact, larger and smaller particles result in non-uniform dispersion and static repulsion and omission of particles in case of electrostatic spray coating.

Advantageously in the composition according to the present invention, a proportion of the flame retardant in polyamide is less than 15% by weight but is higher than 0.1% by weight. In fact, improved flame-proofing cannot be expected if the proportion is under 0.1% by weight. On the other hand, when it exceeds 15% by weight, problems such as discoloration, deterioration in surface appearance and adherence to substrate may occur. A range of 0.5 to 10% by weight is preferable.

The flame retardant can exist in any form or configuration in polyamide composition according to the present invention. For example, the flame retardant is mixed mechanically in powder form to obtain a composition according to the present invention. Or, the flame retardant can be coated on surfaces of polyamide particles or blended therewith. Or, flame retardant can be kneaded into polyamide.

The composition containing the flame retardant according to the
present invention can be prepared by any known technique. For example, the flame retardant and polyamide pellets are blended mechanically in a mixer. Or, polyamide pellets are mixed with flame retardant and then the flame retardant is forced onto surface of polyamide particle by adhesion or welding by means of high energy such as collision energy and shear energy to prepare the composition. Or, flame retardant is kneaded in polyamide and then the resulting mixture is pulverized into a powder composition. Of course, any other method can be used.

Powder coating with the composition according to the present invention can be effected by any known technique including fluidized bed coating, electrostatic spray coating, molten spray coating and mini-coating technique. Continuous coating technique such as turbo coating also can be used. Of course, pre-treatment such as degreasing, shot blasting, primer coating and electrodeposition can be done if necessary.

Generally, a flame retardant possessing lower decomposition temperature is used for electrostatic spray coating technique comparing to fluidized bed coating technique.

Function

The composition of halogen-free according to the present invention can produce a film of little discolored without spoiling performance such as surface appearance and adhesion to substrate, and show homogeneous flame-retardant property.

The composition according to the present invention is applicable to any uses or application including cars, buildings, walls, floor materials, package materials at low temperature and elevated temperature, handles, and panels for fire prevention tank.
Examples

Now, the present invention is described with examples but it is needless to say that the invention is not limited to the examples.

Examples and comparative examples were effected by following procedures and evaluation of flame-retardant and film was effected following methods.

(1) **Coating**

An iron plate of 3.2 mm thick was subjected to antirust and degreasing treatment and was coated with epoxy primer. The primer was coated so that a film after drying had a thickness of 8 to 10 μm. The iron plate was heated in an oven of 400 °C for 3 minutes 50 seconds and was extracted when a surface temperature of iron plate became 280 °C.

Resulting re-treated iron plate was immersed in a fluidized bed filled with a powder coating material containing a predetermined flame retardant to obtain a film sample of predetermined thickness.

(2) **Color difference and gloss of films**

Color difference was determined by measuring L×a×b and calculated \( E \) according to CIE1976. Gloss was determined at an incident angle of 60 °in accordance with DIN67530.

(3) **Flame-retardant property**

Combustion test was carried out in accordance with UL-94.

Example 1, Comparative Example 1

3 % by weight of ammonium polyphosphate was mixed with a powder coating material consisting of polyamide 11 (RILSAN® fine powder product of ATOFINA) by using a Henschel mixer for 5 minutes.

A film prepared from the resulting composition showed excellent
performance of flame-retardant of V-0.

A comparative example containing no ammonium polyphosphate was prepared by the same method. The color difference delta E was such a low value as 0.23. Gloss was 62.6.

Examples 2, 3

Two films were prepared by the same method as Example 1 except that proportions of ammonium polyphosphate were increased to 5 % by weight and 10 % by weight respectively.

The resulting films showed the color differences of 0.261 and 0.91 respectively although the gross was dropped to 53.1 and 27.4 respectively. Both films show superior flame-retardant property of V-0 in UL test.

Comparative Example 2

A film was prepared by the same method as Example 1 except that 5 % by weight of melamine polyphosphate was used as flame retardant.

The resulting film showed the color difference of 1.26. This means that discoloration is higher than a case when 10 % by weight of ammonium polyphosphate (the color difference = 0.91) was used.

Advantages of the Invention

As described above, the composition according to the present invention provides a powder coating material that shows homogeneous flame-retardant property with little discoloration.
CLAIMS

Claim 1 Polyamide-type flame-retardant composition for powder coating consisting mainly of polyamide, characterized in that polyphosphoric acid type compound (excluding melamine phosphate) is incorporated as flame retardant.

Claim 2 The polyamide-type flame-retardant composition for powder coating, wherein said polyamide is polyamide 11 or polyamide 12.

Claim 3 The polyamide-type flame-retardant composition for powder coating, wherein said polyphosphoric acid type compound is ammonium polyphosphate.

Claim 4 The polyamide-type flame-retardant composition for powder coating, wherein a proportion of said flame-retardant is 0.1 to 15 % by weight with respect to the total amount of the composition.