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— *Mit einer Erklärung gemäss Artikel 17 Absatz 2 Buchstabe a; ohne Zusammenfassung; Bezeichnung von der Internationalen Recherchenbehörde nicht überprüft.*

Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

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(54) Title: FILM AND USE THEREOF FOR COATING OBJECTS

(54) Bezeichnung: FOLIE UND IHRE VERWENDUNG ZUR BESCHICHTUNG VON GEGENSTÄNDEN

(57) Abstract:

(57) Zusammenfassung:

FILM AND USE THEREOF FOR COATING OBJECTS

The present invention relates to a film, to its use, to a process for producing coatings on substrates, and to coatings and coated articles.

Self-supporting paint sheets or films for coating planar substrates are known. Their application to the surface of planar substrates does not per se cause any particular difficulties. However, they are of only limited suitability for the coating of three-dimensional articles, especially those which have a pronounced surface profile, such as furniture, industrial components or motor vehicle bodies, for example, since they exhibit only conditional conformation to pronounced surface profiles and, if deformed too greatly, may tear.

Self-supporting paint sheets and films have particular advantages for the user over the production of coatings by means of liquid flow and spray paints, powder slurries, and powder coating materials. Thus they are easy to handle. Their transport and application require no complex transit containers or application and suction equipment. It would therefore be desirable to transfer these known advantages of the self-supporting paint sheets or films to the coating of three-dimensional articles as well.

DE 196 28 966 C1 proposes a process for applying paint film to three-dimensionally curved surfaces of dimensionally stable substrates. In the context of that process, it is proposed to use a paint having a glass transition temperature Tg less than 40°C, in particular less than 30°C, and, during its application to the substrate, to heat the paint film to the glass transition temperature Tg or slightly above it. This softens the paint film and, as a result, it conforms well to the shaped surfaces. A disadvantage with this process is that the paint film must be heated in order to enhance its deformability. As a result of the heat, the paint film itself and also the surfaces to be coated may be damaged. This risk is especially prevalent with plastics surfaces.

It is an object of the present invention to find new paint sheets or films which no longer have the disadvantages of the prior art and which make it possible to coat not only the surface of planar substrates but also three-dimensional articles having a pronounced surface profile without the risk of damage to the paint film or the substrate. A further object of the present invention is to find a new process for coating three-dimensional articles which gives impeccable, firmly adhering, homogeneous coatings of uniform thickness even on highly profiled surfaces.

Accordingly, the new film has been found having

(1.1) a first glass transition temperature T_{g1}, whose maximum loss factor tan δ max lies between -20 and 70°C,

(1.2) a loss factor tan δ > 0.1 at ambient temperature T_{UM} and having

(1.3) at least one further glass transition temperature Tg_n, whose maximum loss factor tan δ max lies above the use temperature T_{NU}, where

(1.4) $T_{UM} \leq T_{NU}$, preferably $T_{UM} < T_{NU}$,

(1.5) the loss factor tan δ at ambient temperature T_{UM} after heating the film and/or exposing it to actinic radiation is < 0.1, and

(1.6) the loss factor tan δ is measured by dynamic mechanical thermoanalysis (DMTA) on homogeneous free films having a thickness of 40 ± 10 μm.

This new film is referred to below as "film of the invention".

Furthermore, the new process for producing a coating by

applying a film to a primed or unprimed substrate has been found in which

(1) a film having

(1.1) a first glass transition temperature Tg_1, whose maximum loss factor tan δ max lies between -20 and 70°C,

(1.2) a loss factor tan δ > 0.1 at ambient temperature T_{UM} and having

(1.3) at least one further glass transition temperature Tg_2, whose maximum loss factor tan δ max lies above the use temperature T_{NU}, where

(1.4) $T_{UM} \leq T_{NU}$, preferably $T_{UM} < T_{NU}$;

(2) is applied at ambient temperature T_{UM},

(3) the applied film is heated and/or exposed to actinic radiation, after which

(4) the loss factor tan δ at ambient temperature T_{UM} is < 0.1.

In the text below, the new process for producing a

coating by applying a film to a primed or unprimed substrate is referred to for the sake of brevity as "process of the invention".

In the light of the prior art, it was surprising that the complex object on which the present invention is based could be simply and elegantly achieved by means of the film of the invention and of the process of the invention. Thus the film of the invention may be laminated without problems onto three-dimensional articles or substrates of comparatively complex shape without said substrates or articles being damaged, let alone tearing. In the course of such application, the film conforms to the unevennesses and/or roughnesses of the articles in both the micro and the macro region and covers them without the film of the invention needing to be heated or subjected to higher pressure for this purpose. Consequently, it is also possible to coat substrates which are thermally sensitive and/or sensitive to the action of mechanical energy, without any damage occurring to the substrates during such coating. Heating and/or exposure to radiation of the film of the invention that has been laminated on gives an impeccable, firmly adhering, flexible and scratch-resistant, homogeneous coating of uniform thickness even on highly profiled and/or very rough substrates.

In accordance with the invention, the loss factor tan δ

is measured by dynamic mechanical thermoanalysis (DMTA) on homogeneous free films having a thickness of 40 ± 10 μm.

The recoverable energy fraction (elastic fraction) in the deformation of a viscoelastic material such as a polymer, for example, is determined by the size of the storage modulus E', whereas the energy fraction consumed (dissipated) in this process is described by the size of the loss modulus E". The moduli E' and E" are dependent on the rate of deformation and the temperature. The loss factor tan δ is defined as the quotient of the loss modulus E" and the storage modulus E'.

The dynamic mechanical thermoanalysis (DMTA) employed for determining the loss factor tan δ is a widely known measurement method for determining the viscoelastic properties of coatings and is described, for example, in Murayama, T., Dynamic Mechanical Analysis of Polymeric Materials, Elsevier, New York, 1978 and Loren W. Hill, Journal of Coatings Technology, Vol. 64, No. 808, May 1992, pages 31 to 33.

The measurements may be conducted, for example, using the instruments MK II, MK III or MK IV from Rheometrics Scientific (Piscataway, New Jersey, USA). For the measurements, the free films of the invention are

produced, for example, by applying the starting materials to substrates and curing them thereon, the substrates in question being substrates to which the starting materials and the films resulting from them do not adhere. Examples that may be mentioned of suitable substrates include glass, Teflon, and particularly polypropylene. Polypropylene has the advantage of ready availability and is therefore normally used as a support material. The free films of the invention may, however, also be produced by other customary and known processes of film production, by calendering or blow molding, for example.

The film of the invention has a first glass transition temperature Tg_1 whose maximum loss factor tan δ max lies between -20 and 70°C. At the same time, in accordance with the invention, the loss factor tan δ at ambient temperatures T_{UM} must be > 0.1. This means that, at ambient temperatures T_{UM}, the film of the invention has a higher plastic fraction of the molecular network, so that, at these temperatures, the film of the invention may be laminated without problems onto primed or unprimed substrates without needing to be heated. In the context of the present invention, the ambient temperature T_{UM} means a temperature of between 0 and 50, preferably 15 and 45, and with particular preference 20 and 35°C, but especially room temperature. In other words, the film of the invention may be applied at

temperatures which normally prevail, depending on season, outdoors or in factory halls, particularly on the line of a motor vehicle plant, or in workshops, particularly a painting workshop, without special heating equipment needing to be provided. In this sense, the ambient temperature T_{UM} is also the application temperature as well.

The film of the invention also has at least one further glass transition temperature Tg_n whose maximum loss factor tan δ max lies above the use temperatures T_{NU}. In accordance with the invention, it is sufficient if the film of the invention possesses a second glass transition temperature Tg_2.

In the context of the present invention, the use temperature T_{NU} is the same as the ambient temperature T_{UM}. In the majority of cases, however, the use temperature T_{NU} lies above the ambient temperature T_{UM} or application temperature. It is especially the case when the coatings produced by means of the film of the invention are exposed to the effect of heat and/or radiation. This is the case, for example, with exterior applications on automobiles or buildings, especially in summer, or in applications in the field of engines, heating systems, lamps or other energy sources.

In accordance with the invention, it is therefore of

advantage if the maximum loss factor tan δ max of the second glass transition temperature Tg_2 and, where appropriate, of any further glass transition temperature Tg_n lies above 70°C, preferably above 80°C, and in particular above 100°C.

The film of the invention is designed in terms of its material composition such that, after heating and/or exposure with actinic radiation at the ambient temperature T_{UM}, it has a loss factor tan δ < 0.1, preferably < 0.05. This means that, after heating and/or exposure to actinic radiation, the molecular network of the film of the invention no longer possesses any plastic fraction at these temperatures.

These characteristics in the film of the invention may be set by, for example, incorporating, into customary and known films, components which on the one hand act as plasticizers and on the other hand may be cured thermally and/or with actinic radiation or removed from the film of the invention by evaporation, for example. Components of this kind are known from the technological fields of thermoplastics and thermosets, photopolymers, adhesives, and coating materials curable thermally and/or with actinic radiation.

Examples of suitable components of this kind are

- water, organic and inorganic acid or bases or water-miscible or -immiscible organic or inorganic solvents;

- customary and known plasticizers;

- compounds which supply free radicals or ions, such as the customary and known initiators of radical or cationic polymerization or photopolymerization;

- customary and known thermosetting systems comprising

  - binders such as linear and/or branched and/or block, comb and/or random poly-(meth)acrylates or acrylate copolymers, polyesters, alkyds, amino resins, polyurethanes, acrylated polyurethanes, acrylated polyesters, polylactones, polycarbonates, polyethers, epoxy resin-amine adducts, (meth)acrylatediols, partially hydrolyzed polyvinyl esters or polyureas, particularly containing thio, amino, hydroxyl, carbamate, allophanate, carboxyl and/or (meth)acrylate groups, and

  - crosslinking agents containing particularly anhydride, carboxyl, epoxy, free and blocked

isocyanate, urethane, methylol, methylol ether, siloxane, amino, hydroxyl and/or beta-hydroxyalkylamide groups;

- radiation-curable binders such as (meth)acryloyl-functional (meth)acrylic copolymers, polyether acrylates, polyester acrylates, unsaturated polyesters, epoxy acrylates, urethane acrylates, amino acrylates, melamine acrylates, silicone acrylates, and the corresponding methacrylates; and/or

- olefinically unsaturated monomers with a functionality of one or more.

In addition, the film of the invention may comprise components which are coloring and/or give rise to other optical effects such as metallic effects, dichroic effects, photochromic effects and/or pearlescent effects and/or which polarize and/or absorb light. Components of this kind as well are known from the abovementioned technological fields and also from optics.

The film of the invention is outstandingly suitable for the process of the invention, in which it is applied to primed or unprimed substrates.

Suitable substrates in accordance with the invention include all surfaces of articles to be coated which are amenable to curing of the paint layer located thereon using heat and/or actinic radiation; that is, for example, articles of metals, plastics, wood, ceramic, stone, textile, fiber composites, leather, glass, glass fibers, glass wool and rock wool or mineral-bound and resin-bound building materials, such as plasterboard panels and cement slabs or roof tiles, and also of composites of these materials.

Accordingly, the film of the invention and the process of the invention are highly suitable for applications in the coating of motor vehicle bodies, furniture, industrial components, including coils, containers, packaging, and everyday articles, and the inside and outside of buildings.

In the context of the coating of industrial components, the film of the invention and the process of the invention are suitable for coating virtually all parts for private or industrial use such as radiators, domestic appliances, small metal parts, hub caps or wheel rims.

In the context of the coating of the inside and outside of buildings, the film of the invention and the process of the invention are outstandingly suitable for the

protective and/or decorative coating of walls, roofs, windows, banisters or doors.

In the context of the coating of motor vehicle bodies, the film of the invention may serve to produce coatings which act corrosion-protectingly, absorb mechanical energy, impart color and/or effect in the sense described above, or have the function of a clearcoat. Suitable primers for the substrates in question include the customary and known electrocoats.

Here in particular it is felt to be a particular advantage of the films of the invention and of the process of the invention that they may be used to outstanding effect to produce multicoat color and/or effect paint systems in which they form the surfacer or the antistonechip primer and/or the color and/or effect basecoat and/or the clearcoat or, alternatively, form the surfacer or the antistonechip primer and/or the solid-color and/or effect topcoat.

In the context of the coating of plastics, the film of the invention and the process of the invention are suitable for producing coatings on primed or unprimed plastics such as, for example, ABS, AMMA, ASA, CA, CAB, EP, UF, CF, MF, MPF, PF, PAN, PA, PE, HDPE, LDPE, LLDPE, UHMWPE, PET, PMMA, PP, PS, SB, PUR, PVC, RF, SAN, PBT, PPE, POM, PUR-RIM, SMC, BMC, PP-EPDM, and UP

(abbreviations to DIN 7728T1). The to plastics may of course also be polymer blends, modified plastics or fiber-reinforced plastics. It is also possible to employ the plastics commonly used in vehicle construction, especially motor vehicle construction. In this context the plastics may be provided, prior to coating, with a water-based primer or may be subjected to a pretreatment with plasma or by flaming.

Following its application, the film of the invention is heated and/or exposed to actinic radiation in the context of the process of the invention.

Heating here may be effected by contacting the film with gases, liquids and/or solids which have been heated to the necessary temperature. Apparatus suitable for this purpose is customary and known. By way of example, mention may be made of fans, dipping baths or presses. Alternatively, heating may be effected by exposure to IR radiation, for which the customary and known radiant heaters or IR lamps are suitable.

Exposure to actinic radiation may be effected using UV light, X-rays and/or gamma radiation and/or corpuscular radiation, particularly electron beams. Radiation sources suitable for this purpose are likewise customary and known.

The two methods may be employed individually in the context of the process of the invention, i.e., the film of the invention is either heated or exposed, or they may be combined with one another. In this case they may be employed simultaneously or alternately.

The consideration as to which procedure is given preference is guided in particular by the material composition of the film of the invention, on the one hand, and by the heat sensitivity and/or light sensitivity of the substrate to be coated, on the other hand. The skilled worker is therefore able to tailor the process precisely to the particular substrate employed and to the particular film of the invention that is used.

The coatings of the invention produced by the process of the invention may be coated with further paint layers. Accordingly, they may also be suitable as primers on the abovementioned substrates. Owing to the advantageous profile of properties of the coatings of the invention, they exhibit particular advantages in this function too, such as good intercoat adhesion and outstanding surface smoothness.

For overcoating, the customary and known powder coating materials, powder slurry coating materials and/or aqueous or solventborne one-component or multicomponent

spray paints, curable thermally and/or with actinic radiation, and/or the films of the invention are suitable. The resultant coatings always exhibit excellent intercoat adhesion.

The coatings of the invention also adhere firmly to the surface of the substrates not only in their planar regions but also in their canted regions. They are free from cracks, pinholes, craters, orangepeel textures, and inhomogeneities. They therefore have an extremely smooth, defect-free surface of extremely high optical quality. They are stable to weathering, hard and scratch-resistant, and flexible enough to exhibit good reflow properties. Owing to their extremely variable material composition, they may at any time easily be adapted to the market requirements. In all of the end uses described above, they display an outstanding profile of properties. Correspondingly, the articles which comprise at least one coating of the invention are of particularly high utility and have a long lifetime.

Claims

1. A film having

(1.1) a first glass transition temperature Tg_1, whose maximum loss factor tan δ max lies between -20 and 70°C,

(1.2) a loss factor tan δ > 0.1 at ambient temperature T_{UM} and having

(1.3) at least one further glass transition temperature Tgn, whose maximum loss factor tan δ max lies above the use temperature T_{NU}, where

(1.4) $T_{UM} \leq T_{NU}$, preferably $T_{UM} < T_{NU}$,

(1.5) the loss factor tan δ at ambient temperature T_{UM} after heating the film and/or exposing it to actinic radiation is < 0.1, and

(1.6) the loss factor tan δ is measured by dynamic mechanical thermoanalysis (DMTA) on homogeneous free paint sheets having a thickness of 40 ± 10 μm.

2. A process for producing a coating by applying a film to a primed or unprimed substrate, characterized in that

(1) a film having

(1.1) a first glass transition temperature Tg_1, whose maximum loss factor tan δ max lies between -20 and 70°C,

(1.2) a loss factor tan δ > 0.1 at ambient temperature T_{UM} and having

(1.3) at least one further glass transition temperature Tg_2, whose maximum loss factor tan δ max lies above the use temperature T_{NU}, where

(1.4) $T_{UM} \leq T_{NU}$, preferably $T_{UM} < T_{NU}$;

(2) is applied at ambient temperature T_{UM},

(3) the applied film is heated and/or exposed to actinic radiation, after which

(4) the loss factor tan δ at ambient temperature T_{UM} is < 0.1.

3. The film as claimed in claim 1 and the process as claimed in claim 2, characterized in that the maximum loss factor tan δ max of the glass transition temperature Tg_2 lies above 70°C.

4. The film as claimed in claim 1 or 3 and the process as claimed in claim 2 or 3, characterized in that T_{UM} is a temperature of between 0 and 50.

5. The film as claimed in one of claims 1, 3 and 4 and the process as claimed in one of claims 2 to 4, characterized in that

- heating of the film is effected by contacting the film with gases, liquids and/or solids and/or by exposure to IR radiation and

- exposure to actinic radiation is effected using UV light, X-rays and/or gamma radiation and/or corpuscular radiation, particularly electron beams.

6. The use of the film as claimed in one of claims 1 or 3 to 5 and of the process as claimed in one of claims 2 to 5 for the coating of primed and unprimed substrates of metals, plastics, wood, ceramic, stone, textile, fiber composites, leather, glass, glass fibers, glass wool and rock

wool, mineral-bound and resin-bound building materials, such as plasterboard panels and cement slabs or roof tiles, and also of composites of these materials.

7. The use as claimed in claim 6, characterized in that the film according to one of claims 1 or 3 to 5 and the process according to one of claims 2 to 5 serves for coating motor vehicle bodies, furniture, industrial components, including coils, containers, packaging, and everyday articles, and the inside and outside of buildings.

8. The use as claimed in claim 6 or 7, characterized in that the films according to one of claims 1 or 3 to 5 and the process according to one of claims 2 to 5 serve to coat particularly motor vehicle bodies with multicoat color and/or effect paint systems in which the films form the surfacer or the antistonechip primer and/or the color and/or effect basecoat and/or the clearcoat or, alternatively, form the surfacer or the antistonechip primer and/or the solid color and/or effect topcoat.

9. Motor vehicle bodies, furniture, industrial components, including coils, containers, packaging, and everyday articles, and the inside

and outside of buildings, comprising at least one coating obtainable using the film as claimed in one of claims 1 or 3 to 5 and/or by means of the process as claimed in one of claims 2 to 5.