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(54) **Eljárás többszínű lakkozással ellátott szubsztrátum előállítására**

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

A fordítást a szabadalmas az 1995. évi XXXIII. törvény 84/H. §-a szerint nyújtotta be. A fordítás tartalmi helyességét a Szellemi Tulajdon Nemzeti Hivatala nem vizsgálta.



Description

The present invention relates to a method for applying a multicolored paint system to a substrate, using a plurality of pigmented coating materials, and also to painted products which can be produced by such a method.

The application of multicolored paint systems to substrates has gained massively in significance within recent years. In the automobile sector, for example, customers are more and more often demanding products distinguished by colored trim strips or by areas marked out by different color relative to a basic color. The realization of multicolored paint systems of this kind, however, generally entails very high complexity and hence also high costs. When carrying out multiple coating operations using different colors, indeed, it is not possible to adhere to the usual sequence of OEM finishing operations. In the case of typical solid-color OEM finishes, as for example in the solid-color OEM finishing of vehicle bodies or bodywork parts, it is usual to apply a coloring basecoat material to the substrate in question, followed by a clearcoat material. This is generally carried out in a process-controlled, timed cycle, with the individual process steps being highly automated and being notable for a very high output.

For the realization of multicolored paint systems, in contrast, the process-controlled cycle has to be interrupted following the application of the coloring basecoat material. The substrate is removed from the process, and one or more further color paints are then applied to the basecoat material applied initially. Before this, of course, the substrate with the basecoat material must be dried and additionally, in a further step, masked. After application of the further color paint or paints has taken place, the masking is removed. The substrates can then be returned to the processing chain described above. The next step, usually, is the concluding application of the aforementioned clearcoat material.

The procedure described is not only inconvenient and time-consuming; it also brings with it further disadvantages. The reason is that conventional OEM finishing processes take place in dust-free, sealed-off coating environments. As a result of the aforementioned removal and return of the substrates, however, dust and dirt are frequently carried into the sealed-off coating environments, and this may result, for

example, in defects in the course of the concluding application of the clearcoat material. Addressing such defects entails further complexity and hence also further costs.

US 4,678,690 refers to decals for decorations in the automotive area. The decals have a protective film adhered to the frontside which has a contrasting appearance against the decal and which is removable from the decal without damage.

From EP 0993878 A1 a method for applying a coloured decoration onto a substrate by using a sheetlike support with release properties is known. According to the method a partially crosslinked coating material is applied to a support with release properties, followed by a coloured decoration which consists of diffused dye. Between the decorated substrate and the decoration an adhesive is arranged.

It was an object of the present invention to provide an alternative technical solution for applying a multicolored paint system to a substrate, with which the problems identified above occur not at all or only to a diminished extent.

This object is achieved by the method having the features of claim 1. Preferred embodiments of the method of the invention are specified in claims 2 to 13.

The method of the invention is used, like the conventional processes mentioned above, for the application of a multicolored paint system to a substrate. Substrates contemplated include more particularly bodies and bodywork parts of motor vehicles. In principle, however, any other substrates desired, such as furniture or electronic devices, for example, may be provided with a multicolored paint system by means of the method of the invention.

A method of the invention always comprises the following steps:

- (1) Applying a first pigmented coating material to the substrate: In this step, the substrate is given a basic color, to which, subsequently, one or more further colors may be applied. The pigmented basecoat material used is usually a waterborne coating material, i.e., a coating material with water as its solvent basis. In principle, however, the first pigmented coating material may also be an alternative solventborne coating material or a powder coating material.

- (2) Drying and/or curing the first pigmented coating material at a drying and/or curing temperature; where the first pigmented coating material used comprises a solvent, this solvent must be removed after the application of the first pigmented coating material. For this purpose the first pigmented coating material is generally exposed to an elevated temperature (the aforementioned drying temperature). Optionally the first pigmented coating material is also brought to a defined temperature (the aforementioned curing temperature), more particularly heated, in order for it to be at least partly cured, where necessary. This is relevant especially when the first pigmented coating material comprises thermally crosslinkable components. In addition, of course, the drying and/or curing step may also encompass curing by means of actinic radiation, more particularly with UV radiation, additionally to or in lieu of the thermal curing. This is relevant especially when the first pigmented coating material comprises radiation-crosslinkable components. In preferred embodiments, the drying temperature corresponds to the curing temperature. Drying and curing may optionally take place simultaneously.
- (3) Applying a second pigmented coating material to the substrate, more particularly with partial recoating of the first pigmented coating material. The second pigmented coating material differs in color from the first pigmented coating material, serving, for example, to provide the aforementioned decorative strips and/or areas marked out by different color. The first pigmented coating material, which usually covers the substrate over a large area, is preferably partly recoated with the second pigmented coating material.

A method of the invention is notable particularly for the fact that the second pigmented coating material is applied using, instead of a conventional paint, a laminate which comprises a carrier on which there is a layer of the second pigmented coating material, this layer being already cured, hence no longer containing any radiation-crosslinkable and/or heat-crosslinkable components or any solvent either. A laminate with an already-cured coating layer of this kind is relatively insensitive to heat; unwanted blistering generally plays no part during its application.

Laminates and coating layers of these kinds are described, for example, in the international patent application filed by the Applicant and bearing the file reference PCT/EP2008/008765 (published as WO2009/024310

A2). They are notable in particular for the fact that the aforementioned carrier is detachable from the coating layer present on it, even if said layer has already undergone thermal and UV curing. The carrier, then, may serve only as a "transfer medium", by means of which a coating material can be transferred to a substrate.

And this is the form of operation used in the present case. For the application of the second pigmented coating material, the laminate is preferably pressed onto the substrate by the side on which the layer of the second pigmented coating material is disposed. The carrier is subsequently removed, then leaving the pigmented second coating layer on the substrate.

The content of PCT/EP2008/006765, more particularly all embodiments relating to the coating materials and laminates described therein, are hereby incorporated by reference as part of the present description.

With particular preference the second pigmented coating material is applied at a temperature which corresponds to the aforementioned drying and/or curing temperature or is even above it. As mentioned, drying and/or curing of the first pigmented coating material in step (2) takes place generally at elevated temperatures. In conventional processes, such drying and/or curing is usually followed by a cooling step, since liquid coating materials, in particular, cannot be applied to heated substrates without blistering. In the context of the present method, no such cooling step is mandatory, and instead the substrate to be painted can be coated directly with the second pigmented coating material while the substrate is still at the drying and/or curing temperature.

In preferred embodiments, after the second pigmented coating material has been applied, the substrate is heat-treated at a heat-treating temperature, more particularly at a temperature between 40°C and 180°C, more preferably between 80°C and 160°C. A heat-treating step of this kind may immediately follow the application of the second pigmented coating material to the substrate which is still hot, being at the drying and/or curing temperature. Alternatively, of course, the second pigmented coating material may also be applied, however, at a temperature below the drying and/or curing temperature. In that case the heat treatment may be necessary in order to ensure sufficient adhesion of the layer of the second pigmented coating material to the layer of the first pigmented coating material.

In preferred embodiments, the laminate employed in the method of the invention may comprise an adhesion-promoting layer, which more particularly is disposed on the second pigmented coating layer. In preferred embodiments, therefore, the second pigmented coating layer is disposed between the adhesion-promoting layer and the carrier. On application, the laminate is then pressed, with the adhesion-promoting layer leading, onto the substrate.

The adhesion-promoting layer is preferably selected such that it is activated at a temperature which corresponds to, or even is above, the aforementioned drying and/or curing temperature or the heat-treating temperature. At room temperature, in contrast, the layer is preferably dry and nontacky. In preferred embodiments it may enter into a durable, firm connection with the dried and/or cured first pigmented coating material only when it is heated at least to the drying and/or curing temperature or to the heat-treating temperature, as, for example, when being contacted with an as yet uncooled substrate from step (2), or during the described heat-treating operation.

In the laminate used, this adhesion-promoting layer is preferably already cured, like the pigmented coating layer. Correspondingly, it preferably no longer contains any groups crosslinkable thermally or by actinic radiation. Its adhesion-promoting properties are preferably activatable exclusively by heating.

The advantages of the procedure according to the invention are obvious. The use of the described laminate, more particularly having the adhesion-promoting layer tailored to the drying and/or curing temperature as per step (2), allows the second pigmented coating material to be applied to the first pigmented coating material without intermediate steps such as the aforementioned cooling step or the abovementioned masking of the substrate and subsequent removal of such masking. This is made possible by the fact that the laminate used can be brought into the particular desired shape by appropriate trimming even before being applied to the substrate. Even complex color patterns and color geometries can readily be applied to the substrate in this way.

In preferred embodiments it is also possible in a method of the invention to use a laminate which comprises a layer of a second pigmented coating material that itself has adhesion-promoting properties, i.e., is able to enter into a firm bond with the first pigmented coating material, without the need for a separate adhesion-promoting layer. Preferably, the

adhesion properties of this layer as well can be activated at a temperature which corresponds to the aforementioned drying and/or curing temperature or is above it (it may be necessary for the laminate used and/or the substrate, heated to the drying and/or curing temperature, to be additionally heated). At room temperature, in contrast, the layer is preferably dry and nontacky.

In particularly preferred embodiments of the method of the invention, not only a second pigmented coating material is applied to the substrate after step (2). It is of course also possible for the substrate to be recoated with one or more further pigmented coating materials. This can be done sequentially or else simultaneously with the application of the second pigmented coating material. For the application of the further pigmented coating material or materials, it is preferred to use at least one further laminate, of the kind described above, i.e., a laminate with a carrier, a pigmented and already-cured coating layer present thereon, and also, optionally, an additional adhesion-promoting layer.

The abovementioned drying and/or curing temperature is preferably in the range between 40°C and 180°C, more particularly between 80°C and 110°C. A temperature within this temperature range is generally sufficient in order to remove any solvent present in the first pigmented coating material and also, optionally, to cure the first pigmented coating material.

Adhesion-promoting layers which can be activated by heating to such a drying and/or curing temperature are known in principle to the skilled person. In the context of the method of the invention, it is particularly preferred for the adhesion-promoting layer used to be a layer of adhesive based on polyurethanes, more particularly based on a polyurethane dispersion. This is so especially when the first pigmented coating material as well is based on a polyurethane, more particularly on a polyurethane dispersion, or has been prepared at least proportionally from such a dispersion.

As pigmented second coating material, the laminates used in a method of the invention preferably likewise have a polyurethane-based coating layer. With particular preference, here as well, a coating material comprising a polyurethane dispersion is used. Suitability is possessed, for example, by polyester-based polyurethane dispersions. This is the case likewise especially when the first pigmented coating material as well is based on a polyurethane, more particularly on a polyurethane

dispersion, or has been prepared at least proportionally from such a dispersion.

Also suitable in principle are the coating layers described in PCT/EP2008/006765 as well, composed of a coating material comprising a double-bond-containing, OH-functional component A and a double-bond-containing, NCO-functional component B, with component A preferably having a solids fraction of between 30% and 100% by weight, a double-bond density of between 2 eq/kg and 5 eq/kg (at a solids fraction of 100%), and an OH content of between 4% and 7% by weight. Component B is generally characterized by a solids fraction of between 30% and 100% by weight, a double-bond density of between 1 eq/kg and 4 eq/kg (at a solids fraction of 100%), and an NCO content of between 4% and 7% by weight. As mentioned above, with regard to preferred features and properties of such a coating material, reference is made to the content of the international patent application with the file reference PCT/EP2008/006765.

Reference may also be made to PCT/EP2008/006765 with regard to suitable carriers. The carrier is preferably a film, more particularly a single-layer film or a multilayer composite film. Suitability is possessed in principle by all films having release properties, more particularly having release properties for polyurethane-based adhesives and coating materials.

The carrier preferably consists substantially of polymeric material, more particularly of fluoropolymers such as ethylene-tetrafluoroethylene (ETFE), polyethylene terephthalate, polyolefin, polycarbonate, acrylic-nitrile-butadiene-styrene (ABS), acrylic-styrene-acrylonitrile (ASA), acrylonitrile-butadiene-styrene/polycarbonate (ABS/PC), acrylic-styrene-acrylonitrile/polycarbonate (ASA/PC), polyacrylate, polystyrene, polycarbonate/polybutylene terephthalate (PC/PBT) and/or polymethyl methacrylate.

With particular preference, a laminate used in a method of the invention has a carrier composed of a biaxially oriented polypropylene film or of a biaxially oriented polyethylene terephthalate film.

The first pigmented coating material is preferably a polyurethane-based coating material, more particularly a liquid coating material. The first pigmented coating material and the second pigmented coating material and/or, optionally, the adhesion-promoting layer are, in preferred embodiments, tailored chemically to one another, thus ensuring optimum

adhesion of the second pigmented coating material to the first pigmented coating material.

Prior to the application of the first pigmented coating material it is possible optionally for an anticorrosion primer to be applied to the substrate. Anticorrosion primers of this kind are known to the skilled person and need not be elucidated further in the context of the present invention.

The same also applies in principle to the clearcoat material, which is applied to the substrate after step (3). Such a clearcoat material is generally a liquid coating material.

In certain particularly preferred embodiments of the method of the invention, the laminate is thermoformed before it is used to recast the first pigmented coating material. This thermoforming may be preferable especially when the substrate to be coated has a nonplanar surface to which the second pigmented coating material and/or one of the further pigmented coating materials is to be applied. The thermoforming of laminates, as described in PCT/EP2009/006765 and used in the context of the present method, is in principle readily possible, provided that thermoformable films are used as carriers. With regard to possible film materials, reference is made to the statements above.

The thermoforming operation on the laminate may take place optionally before the final curing of the pigmented coating material present on the carrier. Since the laminate is generally heated during thermoforming, the coating material may possibly undergo thermal curing during the thermoforming operation. After thermoforming (but before the application of the laminate in the context of a method of the invention), the final curing of the coating material may then take place, by means of actinic radiation, for example.

Substrates provided with a multicolored paint system and producible by a method of the invention or produced by such a method are likewise provided by the present invention. As mentioned above, such substrates

may basically be any possible, conceivable industrial products. Preferably they are automobile bodies or parts thereof.

Further features of the invention will emerge from the example in conjunction with the dependent claims. It is expressly emphasized at this point that all of the optional aspects of the method of the invention or of the substrate of the invention that are described in the present application may be actualized each on their own or in combination with one or more of the further optional aspects described, in any embodiment of the invention. The description below of preferred embodiments serves solely for elucidation and for better understanding of the invention, and should in no way be understood to impose any restriction.

#### Example

A laminate which can be used in a method of the invention was produced by mixing 250 parts by weight of filler paste with 20 parts by weight of butyl glycol, 50 parts by weight of demineralized water, 305 parts by weight of polyurethane dispersion, and 20 parts by weight of polyester polyol emulsion. The resulting mixture was stirred for five minutes, after which 320 parts by weight of pigment paste, 25 parts by weight of polyester polyol emulsion and, for viscosity adjustment, a further 10 parts by weight of demineralized water were added. The resulting paint mixture was then aged for 16 hours, after which its pH was adjusted with dimethylethylamine (DMEA) to a value of between 8 and 9.

Following provision of a biaxially oriented polyethylene terephthalate film, the paint mixture prepared was knife-coated onto one side of this film, and then cured at elevated temperatures.

With a laminate produced in this way it was possible without problems to rescoat a substrate coated with a first pigmented coating material. For this purpose, after the application of the first pigmented coating material, the substrate was dried at a temperature of around 110°C. Immediately after the drying, the laminate produced was applied, with the

paint side leading, to the still-hot layer of the first coating material. Following application, the polyethylene terephthalate film was readily removable.

The film was also readily removable if the laminate was applied to a coating material, this coating material having been dried at between 60°C and 70°C and then cooled to room temperature, and the laminate was subsequently heat-treated at 120°C to 140°C for a short time.



## SZABADALMI IGÉNYPONTOK

1. Lakkozási eljárás többszínű lakkozás szubsztrátumra, különösen karoszeréfa részekre történő felvitelére, amely tartalmazza az alábbi lépéseket

- (1) felvisszünk egy első pigmentált lakkot a szubsztrátumra,
- (2) az első pigmentált lakkot szárítjuk és/vagy kikeményítjük szárítási és/vagy kikeményítési hőmérsékleten,
- (3) felvisszünk egy második pigmentált lakkot a szubsztrátumra, az első pigmentált lakk részbeni átlakkozásával, és
- (4) ez után felvisszünk egy színtelen lakkot a szubsztrátumra, ahol a második pigmentált lakk felviteléhez egy laminátumot alkalmazunk, amely tartalmaz egy hordozót, amelyre fel van vité a második pigmentált lakk egy rétege, amely réteg már ki van keményítve.

2. Az 1. igénypont szerinti eljárás, azzal jellemezve, hogy a második pigmentált lakk felvitelét olyan hőmérsékleten végezzük, amely legalább a szárítási és/vagy kikeményítési hőmérsékletnek felel meg.

3. Az 1. igénypont vagy a 2. igénypont szerinti eljárás, azzal jellemezve, hogy a szubsztrátumot a második pigmentált lakk felvitele után temperáló hőmérsékleten temperáljuk, különösen 40°C és 180°C közötti, különösen előnyösen 80°C és 160°C közötti hőmérsékleten.

4. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a laminátum tartalmaz egy tapadásközvetítő réteget.

5. A 4. igénypont szerinti eljárás, azzal jellemezve, hogy a tapadásközvetítő réteg a szárítási és/vagy kikeményítési hőmérsékleten vagy a temperáló hőmérsékleten aktíválódik.

6. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a (2) lépés után a második pigmentált lakk mellett felvisszünk legalább egy további pigmentált lakkot a szubsztrátumra, ahol ehhez legalább egy további laminátumot alkalmazunk, amely tartalmaz egy hordozót, amelyre fel van vité egy réteg, már kikeményített pigmentált lakk.

7. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a szárítási és/vagy kikeményítési hőmérséklet 40°C és 180°C közötti, különösen előnyösen 80°C és 110°C közötti tartományba esik.

8. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a tapadásközvetítő rétegeként poliuretán alapú ragasztó réteget alkalmazunk.

9. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a laminátum második pigmentált lakként poliuretán alapú lakkréteget tartalmaz.

10. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a ragasztó réteg és/vagy második pigmentált lakkréteg a laminátumban termikusan és/vagy UV sugárzással ki van keményítve.

11. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a szubsztrátumra az (1) lépés előtt korrozóvédő alapozást vité fel.

12. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a laminátumon alkalmazás előtt mélyhúzóást végzünk.