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WATER-DILUTABLE STONE IMPACT PROTECTION PAINT AND COMPENSATION PAINT, THEIR USE AND PROCESSES FOR THEIR PRODUCTION

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(57) **An overspray is the excess of lacquer which during the application of lacquer by spray painting techniques does not hit the article being lacquered but misses the target and is discharged together with the exhaust air from the lacquering zone in order to be transferred, for example in a wet wash out step, to the wash out water of the spraybooths-referred to hereinafter as booth waste water-to wash out the lacquer components present in the overspray.**

Claim

1. A water-dilutable stone chip protection paint, comprising overspray of water soluble base coats and additional binders, pigments, organic solvents and additives.

33. The use of a water-dilutable stone chip protection paint of any one of claims 1 to 26 for lacquering motorcar bodies having an electro-dip primer coat, a second so-called primar surfacer layer and a third layer comprising a water soluble base coat and a clear coat layer, characterized in that the surfacer layer is replaced by a stone chip protection layer of the stone chip protection paint of any one of claims 1 to 26, said protection layer having a thickness of from 10 to 20 µm.

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34. The use of a water-dilutable stone chip protection paint of any one of claims 1 to 26 for lacquering motorcar bodies having an electro-dip primer coat, a stone chip protection layer consisting of the stone chip protection paint of any one of claims 1 to 26 in a thickness of from 10 to 20 µm and a clear coat layer.

35. The use of a water-dilutable stone chip protection paint of any one of claims 1 to 26 for preparing a stone chip protection layer of motorcar bodies having an electro-dip primer coat, a second so-called primar surfacer layer, a third layer comprising a water soluble base coat and a clear coat layer, characterized in that the surfacer layer is replaced by a stone chip protection layer of the stone chip protection paint of any one of claims 1 to 26, said protection layer having a thickness of from 10 to 20 µm.

36. The use of a water-dilutable stone chip protection paint of any one of claims 1 to 26 for preparing a stone chip protection layer of motorcar bodies by applying an electro-dip primer coat (KTL), baking said electro-dip primer coat, applying the stone chip protection paint of any one of claims 1 to 26, drying said stone chip protection paint at a temperature of from 50 to 90°C, applying a base coat, drying said base coat at a temperature of from 50 to 100°C, applying a clear coat, said three layers are baked simultaneously at a temperature of from 130 to 160°C.

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(54) Title: WATER-DILUTABLE STONE IMPACT PROTECTION PAINT AND COMPENSATION PAINT, THEIR USE AND PROCESSES FOR THEIR PRODUCTION

(54) Bezeichnung: WASSERVERDÜNNBARER STEINSCHLAGSCHUTZLACK UND KOMPENSATIONSLACK, IHRE VERWENDUNG UND VERFAHREN ZU DEREN HERSTELLUNG

(57) Abstract

The invention relates to the preparation of a water-dilutable stone impact protection and of a compensation paint and its use and processes for their production, especially in the automobile industry. The water-dilutable stone impact protection paint contains 20 to 60 wt % binder and 2 to 10 wt % pigments and possibly uncoagulated overspray of water-soluble base paints and the compensation paint contains 40 to 80 wt % binder.

(57) Zusammenfassung

Die Erfindung betrifft die Bereitstellung eines wasserverdünnbaren Steinschlagschutzlackes und Kompensationslackes, sowie ihre Verwendung und Verfahren zur deren Herstellung, insbesondere in der Automobilindustrie, wobei der wasserverdünnbare Steinschlagschutzlack 20 bis 60 Gew.-% Bindemittel und 2 bis 10 Gew.-% Pigmente und gegebenenfalls nicht koaguliertes Overspray von wasserlöslichen Basislacken enthält bzw. der Kompensationslack 40 bis 80 Gew.-% Bindemittel enthält.

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SPECIFICATION

The invention relates to the creation of a water-dilutable stone chip protection paint and compensation paint, to their use and to processes for producing the same, especially in the motorcar industry.

A basical problem in the lacquering of surfaces, in particular of motorcar bodies, is the stone chip resistance of the overall lacquering. The stone impact resistance of conventional paints substantially depends on the primer surfacer layer located on the electrocoat layer and having a thickness of about 30 to 40 µm which, on the one hand, equalizes the rough surface of the crude up minor surface inequalities and mainly offers protection motorcar shell to allow subsequent coating with a covering lacquer, fills against mechanical attacks (stone chip protection function).

A conventional motorcar lacquer coating according to the so-called "base coat/clear coat process" consists, for example, of a total of four layers. These four layers are applied one after the other in separate lacquering devices. The first layer, directly located on the car sheet metal, is the electrocoat layer which is applied by electro-dipcoating - mainly cathodic dipcoating (CDC) - for protection against corrosion. The nature of the electro-dipcoating prevents the formation of overspray.

The second layer, located on the electrocoat layer and having a layer thickness of about 30 to 40 µm is the so-called primar surfacer layer which, on the one hand, equalizes the rough surface of the crude motorcar shell to allow subsequent coating with a covering lacquer, levels minor surface inequalities and mainly offers protection against mechanical attacks (stone chip protection function). This layer is substantially produced by electrostatic application of a baking enamel, for example, with electrostatic high rotation bell, followed by baking at temperatures of above 160 °C.

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The third layer, located on the primar surfacer layer, is the base coat layer which imparts to the motorcar body the desired color by virtue of adequate pigments. The water soluble base coat is applied by conventional spray methods.

The fourth and uppermost layer, located on the base coat layer, is the clear coat layer which, analogous to the base coat layer, is applied by conventional spray methods and, on the one hand, imparts the desired lustre and, on the other hand, protects the base coat against environmental factors (UV radiation, salt water etc.).

The object of the invention is to create a stone chip protection paint which meets the requirements of the tests prescribed by the motorcar industry and, at the same time, takes over the function of the conventional primar surfacer layer and the conventional base coat layer.

According to the present invention, there is provided a water-dilutable stone chip protection paint, comprising overspray of water soluble base coats and additional binders, pigments, organic solvents and additives.

An overspray is the excess of lacquer which during the application of the lacquer by spray painting techniques does not hit the article being lacquered but misses the target and is discharged together with the exhaust air from the lacquering zone in order to be transferred, for example in a wet wash out step, to the wash out water of the spraybooths - referred to hereinafter as booth waste water - to wash out the lacquer components present in the overspray.

Preferably, the water-dilutable stone chip protection paint contains from 20 to 60% by weight binders and from 2 to 10% by weight pigments. Preferably, the components to be added to the overspray are added completely or partly in the form of a water-dilutable compensation

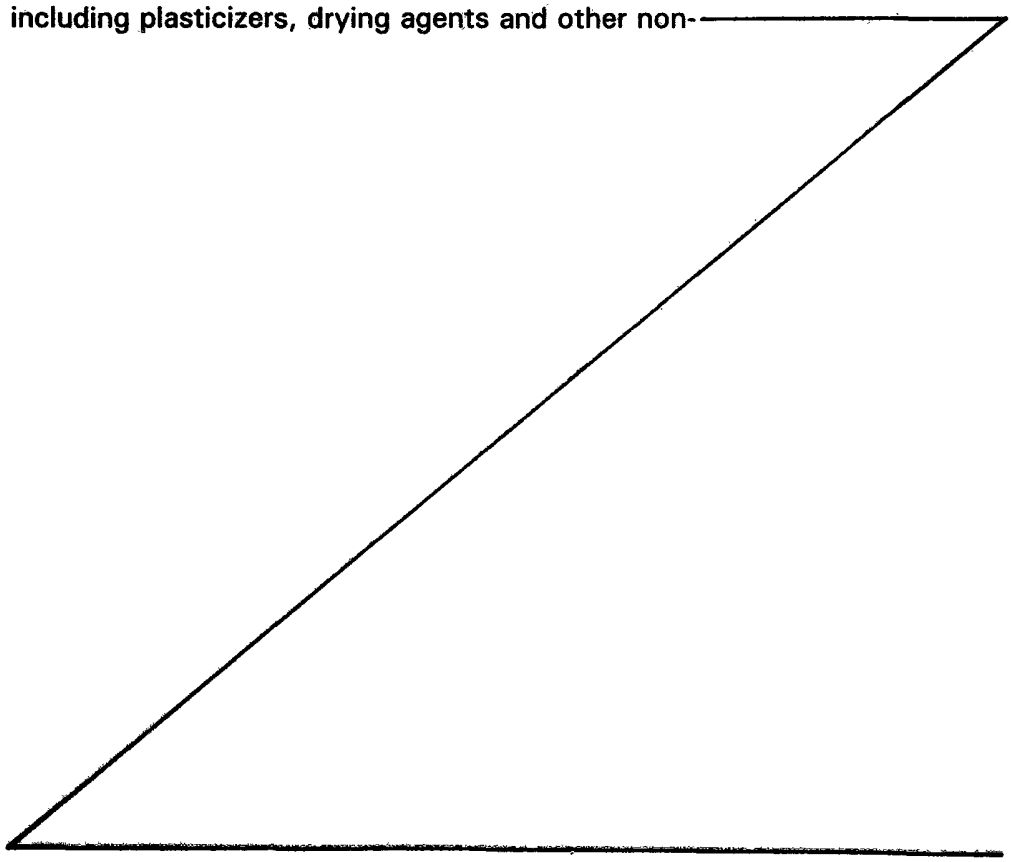
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paint. The water-dilutable compensation paint may contain from 40 to 80% by weight binders. The compensation paint may additionally contain up to 20% by weight pigments.

Pigments, as defined by the present invention, include inorganic or organic multicoloured or achromatic colorants that are practically insoluble in the medium in which they are applied, such as described, for example, in "Glasurit-Handbuch Lacke und Farben", 11th edition, published by Curt R. Vincentz, Hannover 1984, p. 97 - 108, i.e. carbon black titanium dioxide, effect pigments, such as aluminum bronzes, mica pigments and the like.

A binder as defined here and in the following includes substances which bond together similar or different kinds of substances, in particular the non-volatile component of a lacquer without pigment and filler, but including plasticizers, drying agents and other non-



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volatile additives, preferably the water compatible film-forming resins, such as polyester, polyurethane and acrylate resins and the like, as described, for example, in "Glasurit-Handbuch Lacke und Farben", loc. cit. p. 19 - 96 or in H. Wagner, H.F. Sarx "Lackkunstharz e", Carl Hanser Verlag Munich 1972.

In a further embodiment of the invention, the ratio of binders to pigments in the water-dilutable stone chip protection paint is between 5 : 1 and 12 : 1 or between 10 : 1 and 15 : 1 in the case of the water-dilutable compensation paint..
Inasmuch as the water-dilutable stone chip protection paint or the compensation paint contains pigments, the latter can be an effect pigment, in particular an aluminium bronze.

In a preferred embodiment of the invention, the binder of the stone chip protection paint or the compensation paint is a water compatible blocked isocyanate, a polyurethane resin, a polyester resin and/or melamine resin.

In a further embodiment of the present invention, this polyester resin has an average molecular weight of from 5,000 to 10,000, exhibits an adequate number of carboxyl groups which after neutralisation with bases impart to the polyester resin sufficient water-dilutable properties; and contains functional groups, in particular hydroxyl groups by virtue of which the polyester resin is made cross-linkable.

The polyester resin can have a OH number of from 20 to 80, in particular from 30 to 60 and an acid number between 10 and 50, in particular from 15 to 35.
Its glass transition temperature (Tg) may be between -20 and + 30.
In a further embodiment of the invention, the polyester is in particular a polycondensation product of a diol and a dicarboxylic acid in the presence of a component containing more than 2 functional groups.

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The diol is selected from the group consisting of 1,6-hexanediol, neopentyl glycol, 1,4-dimethylolcyclohexane, hydroxypivalic acid neopentyl glycol ester (HPN), perhydrogenated bisphenol A, trimethylolpropane and trimethylolpropane monoallyl ether.

The dicarboxylic acid is selected from the group consisting of adipic acid, phthalic acid, isophthalic acid, hexahydrophthalic acid, tetrahydrophthalic acid or their possible anhydrides, in particular from the group of dimeric fatty acids.

The component containing more than 2 functional groups may be a triol, a tricarboxylic acid, a monohydroxydicarboxylic acid, in particular a dihydroxymonocarboxylic acid, preferably trimellithic acid, trimethylolpropane and dimethylolpropionic acid.

The best properties can be achieved with binders exhibiting elastomeric characteristics after baking. These can be specific polyurethanes in which, due to their segmented structure, a specific sequence of soft and hard segments is observed. Preferred binders are soft polyester resins having a high molecular weight and a high hydroxy-functionality, obtained by polycondensation of dimeric fatty acids and polyalcohols, preferably diols, their crosslinked sites being produced by trifunctional (hydroxy)carboxylic acids. These polyester resins are also used with blocked polyisocyanates or melamine resins as cross-linking agents.

Furthermore, the water-dilutable stone impact-protection paint or compensation paint can additionally contain organic solvents and additives.

The term solvent as used hereinafter includes those organic substances which can dissolve other substances in a physical manner, such as, e.g., lower alcohols, glycol ether, lower ketones, in particular organic solvents which are substantially miscible with water, such as butanol, isopropanol, methylethyl ketone and many others, such as described

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for example, in "Glasurit-Handbuch Lacke und Farben", loc. cit. pages 117 - 138.

Additives are defined as substances that are added in small amounts to other substances, in particular liquid substances, to change their properties in a desired manner or to facilitate their processing. Additives include gloss products, wetting agents, drying agents sedimentation inhibitors, antifloating agents, film-inhibiting agents, leveling agents, release agents, lubricants as well as UV absorbers, biocides, plasticizers, antistats, stabilizers, antioxidants, antiozonants, fillers, viscosity control agents, aging inhibitors, detergents, dispersing agents, defoamers, setting accelerators, solidification retarders or drying agents, as described, e.g., in "Glasurit-Handbuch Lacke und Farben", loc. cit. p. 113 - 117.

The invention also relates to the use of a water-dilutable stone chip protection paint for coating motorcar bodies having an electro-dip primer coat, a second so-called primar surfacer layer, a third layer comprising a water-soluble base coat and a covering layer of clear coat, the primar surfacer layer being replaced by a stone chip protection layer consisting of the stone chip protection paint and having a thickness of from 10 to 20 µm.
In a further embodiment of the present invention, the water-dilutable stone chip protection paint is used for coating motorcar bodies having an electro-dip primer coat, a stone chip protection layer consisting of the stone chip protection paint having a thickness of from 10 to 20 µm and a covering layer of clear coat.

The water-dilutable compensation paint of the present invention is used in mixture with a commercial base coat for coating motorcar bodies having an electro-dip primer coat, a second so-called primar surfacer layer, a third layer consisting of a water-soluble base coat and a covering layer of clear coat, the primar surfacer layer being replaced

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by a mixture of water-dilutable compensation paint and commercial base coat having a thickness of from 10 to 20 µm.

According to another embodiment of the invention, the water-dilutable compensation paint is used in mixture with a commercial base coat for coating motorcar bodies having an electro-dip primer coat, a layer comprising the mixture of water-dilutable compensation paint and commercial base coat having a thickness of from 10 to 20 µm and a covering layer of clear coat.

Thus, the compensation paint serves for conditioning the base coat, i.e. it imparts to a conventional base coat stone chip protection and primar surfacer properties so that the base coat either replaces only the primar surfacer layer (four layer-structure) or the primar surfacer layer and the base coat layer simultaneously (three layer-structure).

This conditioning adapts in particular the adhesion of the stone chip protection layer in such a manner that if a strong mechanical load from an outward source acts on the overall lacquering, which upon using a three layer-coating (i.e. without primar surfacer layer) without the layer of the present invention, would lead to a chipping off of the electrocoat layer, the adherence to the electrocoat layer is controlled to such an extent that, on the one hand, the stone chip protection layer is released from the electrocoat layer, but does not pull the latter from the motorcar sheet metal and, on the other hand, the chipping offs are as little as possible. The latter can be achieved by additives which specifically increase the rebound resilience of the stone chip protection paint. Rebound resistance as used herein means the property by means of which a mechanical impulse (stone impact) is counterbalanced by an elastic deformation. A damage of the material is inhibited thereby.

There are different methods of testing the property of predetermined stability of the pertinent layer, namely of said stone impact protection paint or of a base coat conditioned by said compensation paint, said methods being adapted to the specific field of application, however,

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all of them aim at reproducing the mechanical action as exactly as possible. There are, for example, prescribed tests in the motorcar industry which try to simulate the stone impact by the impact of a shot (Mercedes-Benz AG, lacquer testing apparatus with shot testing apparatus at temperatures of -20 to +50 °C, a shot diameter of from 2 to 4 mm and a shot speed of from 50 to 300 km/h) or a chisel-like testing device (Test VDA 621-428 of BMW-AG) on the finished lacquered surface at exactly defined temperatures (room temperature and -20 °C) and further exactly defined parameters.

In a particularly preferred embodiment of the invention, the overspray from water-soluble base coats contained in the water-dilutable stone impact protection paint of the invention is derived from spraybooth waste water.

A big problem generally encountered in lacquering processes is the waste material, in particular paint sludges. Paint sludges are usually produced when the substantially water-insoluble lacquer components are removed from the booth waste water by coagulation to allow the booth waste water, recovered after sedimentation or separation of the paint sludge, to be recycled for reasons of environmental protection.

In view of the high costs of waste disposal, the lacquer manufacturing and the lacquer processing industries are increasingly interested in applying new methods to avoid this kind of waste. To this end, there are basically two possibilities. On the one hand, one is trying to practically inhibit the formation of an overspray right from the

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beginning by applying specific and more sophisticated lacquering methods. The latter include flow coating, casting, dipcoating, roll coating, coil coating, electro-dipcoating or the like. On the other hand, one is trying to recycle the overspray which is necessarily always formed, for example, when using spray painting techniques. At present, the degree of coating efficiency of this spraying method (air, airless or air mix atomization etc.) is from 20 to 80%, i.e. only from 20 to 80% of the sprayed lacquer hit the surface of the article being lacquered, the rest accrues as overspray.

A conventional water-soluble base coat usually consists of

from 5 to 15 % by weight pigments,
from 10 to 20% by weight binders
0 to 20% by weight organic solvents
0 to 5% by weight additives
40 to 85% by weight water.

A particularly serious problem is the recycling of base coat oversprays. Since, for logistic reasons, the motorcar bodies in a factory are not sprayed serially with the different colors (i.e. not only black on mondays, only white on tuesdays and only red bodies on wednesdays etc.) but several color shades within one hour, one always obtains a variable amount of water-soluble base coat overspray of different colors in the booth waste water. Therefore, the booth waste water has an unsightly shot color from sludgy brown to dirty gray. This excludes the return of this component to the base coat being coated, as proposed in DE-OS 42 13 671.

To date, in all motorcar body lacquering plants, the overspray-containing booth waste waters are converted into a lacquer sludge by coagulating agents. In former times, this lacquer sludge was transported to a waste dump, which is now forbidden by law. Therefore, nowadays this coagulate or paint sludge, which still contains about 50% by weight water, is reprocessed, after removal of

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the main amount of water, drying in rotating tubular kilns and grinding to form granulates or powder, and is reutilized for other purposes. This means in the case of the granulates, that they are disposed of by the so-called "thermal recovery", i.e. incineration of special waste. The energy recovered thereby does neither compensate the loss of material nor the expenditure of method and capital.

The recovery of the booth waste water-overspray in the sense of a recycling to the spraying process, i.e. a recovery on a higher level, is only possible in the processing of water thinnable lacquers. Water thinnable lacquers are those systems which contain, beside the conventional lacquer components, water-dispersible binders and which have water as main solvent. When using water thinnable lacquers in spray coating techniques, one has the possibility of precipitating the overspray in the booth waste water in such a manner that coagulation does not take place. Thus, the booth waste water becomes a very diluted water thinnable lacquer which can be depleted from excess water by suitable methods and be reutilized as lacquer. Thus, DE-OS 42 13 671 describes a process for recovering the overspray from aqueous coating compositions during spray coating in water dripping spraybooths by means of ultrafiltration which allows to concentrate the enriched booth waste water (retentate) to a solids content of up to 35% by weight. DE-OS 42 07 425 describes a process for recovering the lacquer overspray of aqueous lacquers during spray coating by ultrafiltration and sebsequent electrophoresis. Further processes for recovering water thinnable lacquer oversprays are described in DE-OS 34 28 300, CH-OS 1656/59, DE-OS 41 33 130 and DE-OS 42 02 539.

It has also been contemplated to recycle the booth waste water until a water thinnable lacquer concentration is obtained in said booth waste water which permits the direct use of the latter as thinnable lacquer. JP-PS 49 51 324 teaches to increase the concentration of lacquer in the lacquer-containing precipitate by removal of water from the entire

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booth waste water to such an extent that this precipitate can be reutilized for color spray painting. However, practical tests showed that a concentration of thinnable lacquers in booth waste water to a solids concentration of more than 2% by weight results in that the overspray is no longer completely washed out and the discharged exhaust air contains more overspray than is prescribed by the law (technical instructions on air quality control). The solids concentration refers to the overall amount of non-volatile lacquer components, such as pigments, binders, additives etc., expressed as weight percent, based on the total content of all lacquer components.

DE-OS 42 13 671 and 41 33 130 teach methods of recovering the oversprays of aqueous coating compositions during spray coating in spray booths according to which part of the liquid circulating in the ultrafiltration cycle is used as aqueous coating composition for spray coating. This circulating liquid is alway added to the same spraying composition from which overspray it is obtained.

The overspray comprising aqueous base lacquers for producing a stone impact protection layer which dries at from 50 to 90 °C is used according to the invention between the electrocoat layer and the base lacquer layer.

For the purposes of the invention, the overspray can be recovered by any conventional method. Its accumulation can be effected, for example, according to the lacquer recovery methods described in I-Lack 61 (1993), p. 425-428 (washer device, recovery wall, recovery belt, Relas lamella-recovery system). The overspray is preferably recovered in a condition allowing its use according to the invention by means of any prior art wet wash out method. This wet wash out results in an accumulation of the overspray in the booth waste water.

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With respect to the composition of the individual lacquer components, the overspray in the booth waste water has a different composition from the base coat since, for example, the evaporation of the volatile organic solvents is quicker and, therefore, escape to the atmosphere together with the exhaust air from the spraybooth.

The booth waste water normally consists of
form 0.1 to 1.5% by weight pigments,
from 0.1 to 2.0% by weight binders,
from 0 to 2.0% by weight organic solvents,
from 0 to 0.5% by weight additives and
from 94 to 99.8% by weight water.

Booth waste water containing an overspray which consists of water-soluble base coats of different colors is preferably used for the purposes of the invention.

This booth waste water is preferably used in a water-depleted upgraded form in the light of the invention. This upgrading by water depletion can be effected by any separation procedure familiar to the expert, such as concentration by vaporization, concentration by boiling in vacuo, freezing out, centrifugation or freeze drying. An upgrading of the booth waste water is usually conducted by ultrafiltration or a combination of ultrafiltration and electrophoresis (DE-OS 42 97 425).
This upgraded booth waste water has a solids concentration of from 10 to 35% by weight. In the upgrading of overspray absorbed in water, changes in respect of the composition of the concentrate because, for example, preferably water-insoluble and high molecular weight components such as pigments and binders are retained by ultrafiltration while the water soluble and low molecular weight components, such as solvents, melamine resins and neutralizing agents preferably are transferred to the permeate. The water depletion

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can also result in a change of the properties of the paint components, such as color shade and rheology.

The upgraded booth waste water usually consists of

from 2 to 12% by weight pigments,
from 4 to 18% by weight binders,
from 0 to 5% by weight organic solvents,
from 0 to 0.8% by weight additives,
from 64 to 94% by weight water.

Thus, by virtue of the production of the stone chip protection paint of the present invention, a big problem of the spray coating technique according to the "base coat/clear coat" method is solved because all of the overspray accrued in the spray coating of the base coat layer in the booth waste water can be utilized. This means that it is no longer necessary to coagulate booth waste water and, consequently, paint sludge is not obtained when the base coat layer is applied.

In addition, this means that both the base coat overspray as well as the overspray of the stone chip protection paint recovered therefrom can be united in one booth waste water.

A basical advantage of using booth waste water for producing stone chip protection paint is that the booth waste water may also contain different color shades of the water-soluble base coats and can, nevertheless, be reutilized as valuable material.

A further particular advantage in replacing the conventional filler layer by the stone chip protection layer of the present invention consists in that the baking of this primar surfacer layer can be dispensed with. The stone chip protection layer of the present invention dries at a temperature of between 50 and 90 °C and, consequently, necessitates, for example, only a drying or a predrying with infrared radiation. This means a considerable saving of energy and time. Moreover, it is not necessary to apply the stone chip protection layer of the present

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invention with the same layer thickness as the primar surfacer layer; it is enough if said stone chip protection layer has a thickness between 10 and 20 µm to possess the same mechanical properties as the conventional primar surfacer layer. This also means a considerable saving of material.

A further advantage over the prior art is that two instead of three booth waste water cycles have to be installed. The recycling of the clear coat, e.g. by ultrafiltration, makes it possible to run for the first time a motorcar standard lacquering which is completely free of paint sludge. When water borne clear coats are used, it is even possible to run the process with only one booth waste water cycle if the coating efficiency of the water borne clear coat application is optimized by suitable methods such that the accrued amounts of overspray do not exceed the demand for the stone chip protection paint of the present invention. Besides, the demand for stone chip protection paint can be controlled by varying the layer thickness, (in particular heightening).

In case the stone chip protection paint, manufactured according to the invention from the concentrated booth waste water, does not exhibit the desired protective properties against mechanical load acting on the overall lacquering from outside, it can be conditioned as specified in the invention.

This conditioning is effected by adding the components necessary for the desired properties of the stone chip protection layer. It can also be advantageous to remove the effect pigments, partly or completely.

The object of this conditioning is, in particular, to adjust the adhesion of the stone impact protection layer in such a manner that if a strong mechanical load acts on the overall lacquering from outside, which without the stone chip protection paint of the invention and the use of a three-layer lacquering (i.e. without primar surfacer layer) would entail a chipping off of the electrocoat, the adhesion to the electrocoat

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layer is adapted in such a manner that, on the one hand, the stone chip protection layer is released from the electrocoat layer but the latter is not torn off therewith from the motorcar body and, on the other hand, the chipping offs are as small as possible. The latter can be achieved by additives which increase the rebound resilience of the stone chip protection paint to a predetermined degree. The term rebound resilience stands for the property by means of which a mechanical impulse (stone impact) is compensated by an elastic deformation. A damage of the material is thus inhibited.

The above-mentioned mechanical loads acting on the overall lacquering from outside may involve any kind of mechanical action, such as, for example, stone impact on motorcar lacquerings, frictional contact or impact contact between lacquered articles or any kind of objects on laquered surfaces.

For conditioning the mechanical properties of the stone chip protection paint of the present invention, binders, such as a water compatible blocked isocyanate, a melamine resin, a polyurethane resin or polyester resin; organic solvents, pigments or additives can be used as suitable components.

These components can be added to the stone chip protection paint alone or in any combination or also as compensation paint having a solids concentration of from 20 to 80% by weight.

This compensation paint contains all or parts of the components necessary for conditioning the desired mechanical properties of the stone impact-protective layer.

Thus, a stone chip protection layer cycle is formed according to the invention, to which base coat overspray and compensation paint are periodically added.

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Subsequent to the conditioning of the upgraded booth waste water an equilibrium is established after some time within said cycle which can be maintained by the appropriate amount of compensation paint, which can be easily determined by the expert.

The particular advantage in the use of the compensation paint resides in that all components can be added to the stone chip protection paint, adapted to the pertinent base coat system, to the corresponding overspray or to the booth waste water, and that in a single mixing procedure directly in the spray coating plant or its direct neighbourhood. Therefore, the concentrated booth waste water, which can contain up to 90% water, must not be transported from the lacquer processing plant to another place where it is tested in respect of the properties required for the stone chip protection layer and, if desired, conditioned by the method of the present invention, but all these procedures can be done in the same place where the lacquering is conducted.

The higher the concentration of the compensation paint , the less water must be removed from the booth waste water.

The process of lacquering motorcar bodies comprises applying an electro-dipcoat primer (CDC), baking the same, applying the stone chip protection paint of the present invention, drying the same at 50 - 90 °C, applying a base lacquer, drying the same at 50 - 100 °C, applying a clear coat and subsequently jointly baking the three lacquer layers at 130 - 160 °C.

The stone chip protection paint of the present invention can be used for lacquering all solid, plane or non-planar smooth or uneven metallic surfaces which are coated according to the above-specified "base coat /clear coat process" and which are to be protected against mechanical load outwardly acting on the overall lacquer, said protection paint being located between the electrocoat layer and the base coat layer. Smooth metallic surfaces, such as occur in the

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lacquering of plants, apparatuses, windows, in particular motorcars (cars, trucks, bikes etc.) are mainly involved.

The following examples will illustrate the invention.

EXAMPLES

Preparation Example A of a Polyester Resin

In a reactor provided with stirrer, condenser and heater, as well as a packed column, 1187 g 1,6-hexanediol and 1473 g dimeric fatty acid (Pripol 1009 of the UNICHEMA company) are weighed and heated such that the head temperature of the column does not exceed 100 °C. The maximum esterification temperature amounts to 220 °C. When the acid number is below 5, cooling to 150 °C is effected and 1499 g admerginic acid (an addition product of linseed oil fatty acid and maleic anhydride, commercial product of the HARBURGER FETTCHEMIE) are weighed. Heating is again conducted in such a manner that the head temperature of the column does not exceed 100 °C. The maximum esterification temperature amounts to 220 °C. Cooling is effected at an acid number of 38, followed by dilution with 1658 g Butyl glycol. A polyester having a solids content of 70% and a hydroxyl number of 57 is recovered.

Preparation Example B of a Polyester Resin

In a reactor provided with stirrer, condenser and heater, as well as a packed column, 598 g dimethylolcyclohexane, 3098 g dimeric fatty acid (pripol 1009 of the UNICHEMA company) and 371 g dimethylolpropionic acid are weighed and heated in such a manner that the head temperature of the column does not exceed 100 °C. The maximum esterification temperature amounts to 220 °C. Cooling is

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effected at an acid number of 30, followed by dilution with 1651 g butyl glycol. A polyester having a solids content of 70% and a hydroxyl number of 30 is obtained.

Example 1 (Compensation Paint)

337 parts of a polyester resin of preparation example A are mixed with a blend of 227 parts of fully desalted water and 12 parts dimethylethanol amine with stirring. 39 parts of the commercial melamine resin Luwipal LR 8852 are added thereto with further stirring. The pH value is 9.06. The viscosity is adjusted by fully desalted water to 130 sec., measured in DIN 4 (German standard) cup.

Example 2 (Compensation Paint)

404 parts of the polyester resin of preparation example B are mixed with a blend of 457 parts of totally desalted water and 10 parts dimethylethanol amine with stirring. 47 parts of the commercial melamine resin Luwipal LR 8852 are added thereto with further stirring. The pH value is 9.06, The viscosity is adjusted by fully desalted water to 130 sec., measured in DIN 4 cup.

Example 3 (Compensation Paint)

206 parts of the polyester resin of preparation example B are mixed with stirring with a blend of 289 parts totally desalted water and 7.5 parts dimethylethanol amine. 298 parts of the blocked isocyanate Bayhydrol LS 2050 of the Bayer AG company Leverkusen are added thereto with further stirring. The pH value is adjusted with an aqueous 10%-dimethylethanol amine solution to 8.5. The viscosity is adjusted by fully desalted water to 130 sec., measured in a DIN 4 cup.

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Example 4 (Reprocessing of Overspray)

A laboratory spray booth having a water capacity of 250 liters was filled with fully desalted water. Five different water base coat-color shades, prepared as described in European patent 502 934, were sprayed with a flow beaker spraying gun. About 2 to 3 kg of each color shade were consumed until the solids content of the booth recycling water has increased to 1%.

The so-obtained booth water was upgraded to a solids content of 18% by ultrafiltration.

Example 5 (Stone Chip Protection Paint)

2 parts of the commercial melamine resin Cymel 327 are added to 390 parts of the retentate of the above-described reprocessing with stirring. 268 parts of the compensation paint of example 1 are added to this blend and the viscosity is adjusted to 35 sec. by fully desalted water.

Example 6 (Stone Chip Protection Paint)

78 parts of each of the same five water base lacquer-color shades which were used to mulate the overspray (as described in example 4) are mixed with stirring. 268 parts of the compensation paint of example 1 is added thereto, likewise with stirring. After adjusting the pH value to between 9.0 and 9.1, the viscosity is adjusted by fully desalted water to 35 sec.

The stone chip protection paints were sprayed according to conventional methods on phosphated sheet steels coated with a commercial electro-dipcoat. After a flash off time of 3 minutes, drying was conducted at three different temperatures. One part of the sheets was dried for 10 minutes at 100 °C, the second part for 10 minutes at 130 °C and the third part for 10 minutes at 105 °C. The dry layer

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thicknesses were between 14 and 19 µm. Thereafter, all sheets were overpainted in a conventional manner with commercial water base coat and 2 components clear coat comprising mainly isocyanate.

Example 7 (Base Coat with Integrated Stone Impact Protection Paint)

100 parts of a metallic base coat with a silver color shade, prepared as described in European Patent 502 934, were blended with 135 parts of the compensation paint of example 3 with stirring, and adjusted to a viscosity of 45 sec. (DIN 4).

The so-modified base coat is sprayed on phosphated sheet steels coated with a commercial electro-dipcoat and after a flash off time of 5 minutes is overpainted with clear coat. The layer thickness of the first modified base coat layer was 9 µm and that of the second unmodified layer 7 µm.

All sheets exhibited a good appearance, comparable to conventional standards.

The sheets were subjected to a stone impact test, as is common at Mercedes Benz AG. To this end, the test sheets were first cooled to -20 °C and were shot with a steel ball having a diameter of 3 mm at a speed of 250 km/h. A penetration up to the sheet should not occur thereby and the chipping offs should not be greater than 8 mm^2. All test sheets passed this test.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A water-dilutable stone chip protection paint, comprising overspray of water soluble base coats and additional binders, pigments, organic solvents and additives.

2. The water-dilutable stone chip protection paint of claim 1 comprising booth waste water with uncoagulated overspray of water soluble base coats.

3. The water-dilutable stone chip protection paint of claim 1 or 2 comprising booth waste water upgraded to a solids concentration of from about 10 to 35% by weight, as well as additional binders, pigments, organic solvents and additives.

4. The water-dilutable stone chip protection paint of any one of the preceding claims containing uncoagulated overspray of water soluble base coats of different color shades.

5. The water-dilutable stone chip protection paint of any one of the preceding claims wherein the additional binder is a water compatible blocked isocyanate, a polyurethane resin, polyester resin or melamine resin.

6. The water-dilutable stone chip protection paint of any one of the preceding claims wherein the solvents being added are partly or completely miscible with water.

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7. The water-dilutable stone chip protection paint of any one of the preceding claims characterized in that it does not detach itself upon predetermined mechanical load or only from the electrocoat layer.

8. The water-dilutable stone chip protection paint of any one of the preceding claims characterized by having a high rebound resilience.

9. The water-dilutable stone chip protection paint of any one of the preceding claims wherein the binder has elastomeric properties after baking.

10. The water-dilutable stone chip protection paint of any one of the preceding claims characterized in that it comprises from 20 to 60% by weight binders and from 2 to 10% by weight pigments.

11. The water-dilutable stone chip protection paint of claim 10 wherein the ratio of binders to pigments is between 5 : 1 and 12: 1.

12. The water-dilutable stone chip protection paint of any one of the preceding claims wherein said pigment is an effect pigment, in particular aluminum bronze.

13. The water-dilutable stone chip protection paint of any one of the preceding claims wherein said binder is a water compatible blocked isocyanate, a polyurethane, polyester and/or melamine resin.

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14. The water-dilutable stone chip protection paint of claim 13 wherein said polyester resin has an average molecular weight of from 5,000 to 10,000; exhibits sufficient carboxylic groups which impart to the polyester resin, after neutralization with bases, sufficient water-dilutable characteristics; and contains functional groups, in particular hydroxyl groups, making the polyester resin crosslinkable.

15. The water-dilutable stone chip protection paint of claim 13 or 14, wherein said polyester resin has a OH number of from 20 to 80, in particular of from 30 to 60 and an acid number of from 10 to 50, in particular of from 15 to 35.

16. The water-dilutable stone chip protection paint of any one of claims 13 to 15 wherein said polyester resin has a glass transition temperature (Tg) of from -20 to +30 °C.

17. The water-dilutable stone chip protection paint of any one of claims 13 to 16 wherein the polyester is a polycondensation product of a diol and a dicarboxylic acid in the presence of a component containing more than 2 functional groups.

18. The water-dilutable stone chip protection paint of claim 17 wherein the diol is selected from the group consisting of 1,6-hexanediol, neopentyl glycol, 1,4-dimethylolcyclohexane, hydroxypivalic neopentyl glycol ester (HPN), perhydrogenated bisphenol A, trimethylolpropane and trimethylolpropane monoallyl ether.

19. The water-dilutable stone chip protection paint of claim 17 or 18 wherein the dicarboxylic acid is selected from the group consisting of adipic acid, phthalic acid, isophthalic acid, hexahydrophthalic acid, tetrahydrophthalic acid or their possible anhydrides, in particular from the group of dimeric fatty acids.

20. The water-dilutable stone chip protection paint of any one of claims 17 to 19 wherein the component containing more than 2 functional groups is a triol, a tricarboxylic acid, a monohydroxydicarboxylic acid, in particular a dihydroxymonocarboxylic acid.

21. The water-dilutable stone chip protection paint of claim 20 wherein said component containing more than 2 functional groups is trimellithic acid, trimethylolpropane, in particular dimethylolpropionic acid.

22. The water-dilutable stone chip protection paint of any one of the preceding claims additionally comprising organic solvents and additives.

23. The water-dilutable stone chip protection paint of any one of the preceding claims wherein the components to be added to the overspray are added completely or partly in form of a compensation paint.

24. The water-dilutable stone chip protection paint of claim 23 wherein the compensation paint comprises from 40 to 80% by weight binders.

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25. The water-dilutable stone chip protection paint of claim 23 or 24 wherein the compensation paint additionally comprises up to 20% by weight pigments.

26. The water-dilutable stone chip protection paint of any one of claims 23 to 25 wherein the ratio of binders to pigments in the compensation paint is between 10 : 1 and 15 : 1.

27. A process for the preparation of a water-dilutable stone chip protection paint of any one of claims 1 to 26 wherein overspray of water soluble base coats resulting from the application of the coat by spray painting techniques is used.

28. The process of claim 27 wherein uncoagulated overspray of water soluble base coats is used.

29. The process of claim 27 or 28 wherein spraybooth waste water is used, concentrated to a solid content of from 10 to 35% by weight by removal of water and comprising uncoagulated overspray of water soluble base coats.

30. The process of any one of claims 27 to 29 wherein overspray of water soluble base coats having different color shades is used.

31. The process of any one of claims 27 to 30 comprising adding the necessary components in the form of a compensation paint having a solid concentration of from 20 to 80% by weight.

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32. The process of claim 31 characterized in that the necessary components are binders, pigments, organic solvents and additives.

33. The use of a water-dilutable stone chip protection paint of any one of claims 1 to 26 for lacquering motorcar bodies having an electro-dip primer coat, a second so-called primar surfacer layer and a third layer comprising a water soluble base coat and a clear coat layer, characterized in that the surfacer layer is replaced by a stone chip protection layer of the stone chip protection paint of any one of claims 1 to 26, said protection layer having a thickness of from 10 to 20 µm.

34. The use of a water-dilutable stone chip protection paint of any one of claims 1 to 26 for lacquering motorcar bodies having an electro-dip primer coat, a stone chip protection layer consisting of the stone chip protection paint of any one of claims 1 to 26 in a thickness of from 10 to 20 µm and a clear coat layer.

35. The use of a water-dilutable stone chip protection paint of any one of claims 1 to 26 for preparing a stone chip protection layer of motorcar bodies having an electro-dip primer coat, a second so-called primar surfacer layer, a third layer comprising a water soluble base coat and a clear coat layer, characterized in that the surfacer layer is replaced by a stone chip protection layer of the stone chip protection paint of any one of claims 1 to 26, said protection layer having a thickness of from 10 to 20 µm.

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36. The use of a water-dilutable stone chip protection paint of any one of claims 1 to 26 for preparing a stone chip protection layer of motorcar bodies by applying an electro-dip primer coat (KTL), baking said electro-dip primer coat, applying the stone chip protection paint of any one of claims 1 to 26, drying said stone chip protection paint at a temperature of from 50 to 90°C, applying a base coat, drying said base coat at a temperature of from 50 to 100°C, applying a clear coat, said three layers are baked simultaneously at a temperature of from 130 to 160°C.

Dated this 30th day of September, 1998

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/DE 95/00767

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D175/06 C09D5/36 B05B15/12

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 6 C09D B05B

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP,A,0 590 484 (BASF) 6 April 1994 see page 2, line 54 - page 9, line 3; claims; examples	1-16
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 October 1995	18. 10. 95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,	

INTERNATIONAL SEARCH REPORT

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