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(54) Titre : STRATIFIE DECORATIF ET SON PROCEDE DE PRODUCTION
(54) Title: DECORATIVE LAMINATE AND METHOD FOR PRODUCING THE SAME

(57) Abrégé/Abstract:
The invention relates to a decorative laminate with an abrasion-resistant surface coating for laminate floor boards or the like, which is characterized in that the thermoset resin mass that forms the resin impregnation of the decorative web and the abrasion-resistant surface resin layer that is materially integral with it with a closed surface is formed with a thermosettable synthetic resin and conventional additives and/or adjuvants, the synthetic resin mass as a component containing a mixture integrated into the resin mass or such a compound of at least one wax or wax blend based on a polyalkylene polymer and at least one polyvinyl pyrrolidone, in that the particles of the abrasion-resistant hard material in the surface layer are concentrated essentially only directly bordering the decorative web surface and in the vicinity thereof, and in that the covering density of the particles of abrasive material located in the surface layer in the same -- proceeding from a high value directly on the decorative web -- toward the outer surface of the surface layer, following a steep negative gradient, drops to a value of zero.

Abstract:

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in that the particles of the abrasion-resistant hard material in the surface layer are concentrated essentially only directly bordering the decorative web surface and in the vicinity thereof, and

in that the covering density of the particles of abrasive material located in the surface layer in the same -- proceeding from a high value directly on the decorative web -- toward the outer surface of the surface layer, following a steep negative gradient, drops to a value of zero.

Decorative Laminate and Method for Producing the Same

This invention relates to a decorative laminate with an abrasion-resistant surface coating for laminate bodies that have been or are to be coated with it, especially laminate floor boards or panels based on wood materials..

Furthermore, this invention relates to the production of the new decorative laminate that has an abrasion-resistant surface coating and that is intended for floor boards, panels, and the like.

The wide popularity of laminate floors according to EN 13329 is due to, among others, the especially good capacity of these floor coverings to be cleaned. This in turn is a result of the absence of pores of the surface or the outside of its surface coating, which is generally labelled with the technical expression "closed."

Actually "closed" surfaces were made possible in the past by use of so-called "classic" overlays. Such classic overlays consist of thin, especially transparent special papers that are impregnated with duroplastic resins, such as especially melamine resins. These papers are located on or over the surface film and wear film of the decorative web and are pressed with the latter with the decorative web and ultimately with the substrate based on a wood-based material into the laminate intended for laying of floors and are of decisive importance for ease of cleaning of laminate floors. By using classical overlay films, especially in the form of overlay paper webs, however, the gloss of the surface or surface layer of the decorative film is inevitably reduced because as a result of the presence of the fibers in the overlay film, an inevitable and clearly perceptible haziness of lines, patterns, designs, etc., and a certain attenuation and clouding of the color and graphic impression of the surface decoration occur.

If, however, the classic overlay that is present generally in the form of a coating resin-impregnated overlay paper is omitted, which has been attempted again and again for some time, and which will be considered in more detail below, "open pores" of the surface layer arise that ultimately lead to irreversible soiling of the laminate surface that in any case significantly degrades the optical effect, which is especially a problem in laminate floors and could not be avoided in the past.

Another completely unacceptable consequence of omitting the overlay consists in the danger that in the production of laminates for various purposes, and especially for floors, the surfaces of the pressing sheets used in the so-called short contact process or of the pressing belts used in continuous laminate production are damaged or destroyed. For this reason, in the past in daily operating practice with currently conventional high production rates, it was in fact not possible to carry out production of highly abrasion-resistant laminates undisrupted over time intervals that are as long as possible without using classic overlays that had proven themselves in practice, as known in the art. In particular, in spite of various approaches to solving this serious problem that arises in abrasion-resistant laminate surfaces without overlay films, it has not been possible to date to fully protect the surface-chrome-plated, highly sensitive pressing sheets or continuous pressing belts of the production lines against the aforementioned mechanical damage or possibly even against destruction by the particles of abrasive substance protruding from the surface layer of decorative laminates that have been finished to be abrasion-resistant.

The fact that numerous attempts have been made to produce surface layers of laminates that are lastingly abrasion-resistant for their use and application is not inherently significant since the abrasion-resistance values required according to EN 13329 can be achieved to a comparable degree with decorative films without overlay papers when they have been finished only with particles of abrasive substances that ensure the required wear resistance. For this reason, therefore, the use of classic overlays in the production of laminates for floors is not necessary to achieve the abrasive resistance values required by EN 13329. However, the classic overlays, as stated above, are of quite decisive importance for the protection of pressing sheets or continuous pressing belts against the harmful effect of the particles of abrasive substances contained in the surface layer of the decorative laminate to be produced - for the most part they are corundum particles.

Almost all attempts to date to produce decorative films finished to be more highly abrasion-resistant by means of continuous pressing belts or pressing sheets without using classical overlays have failed due to the surface damage or even destruction of the chrome plating of the indicated belts or sheets and/or of the pressing structures impressed on them, caused by the medium of abrasive substance that is present in the surface layer and that increases the abrasion resistance.

Another problem of surface coatings without overlay paper that likewise has not been solved to date is that the fibers of the overlay papers reliably prevent later crack formation in the setting hard layer of resin precondensates, especially melamine formaldehyde precondensates, but that in practice all attempts to bypass the classic overlays with respect to the desired absence of cracking have not led to a permanent solution that has in fact been satisfactory to date.

One approach that may be technologically feasible to dispensing with the protective overlay foils or films that are provided for protection of the pressing sheets or belts in the production of laminates, e.g., for floors, would be to use so-called structuring papers, as disclosed in, e.g., DE 101 24 710 A1. The latter would replace the correspondingly structured surfaces of the pressing sheets or continuous belts in laminate floor production and in their place impart the surface structure desired in each case to the laminate and protect the chrome-plated continuous belt itself.

As practice has shown, however, the use of structuring papers is associated with a major decrease of the quality of the laminates obtained using them, which relates not only to the structuring itself. As a result of the inhibition of heat transfer from the pressing sheet or from the continuous belt of the continuous press that is caused by the intermediate paper layer, the production rate is greatly reduced or else the quality of the laminate surface is greatly degraded as the feed rate remains the same.

Of course, the problem of cracking furthermore remains unresolved by the use of structuring papers.

A large number of processes for producing laminates provided with a surface coating to which particles of abrasive substances have been applied, without overlay paper, film or foil have become known in the art that differ from one another both with respect to the composition of the resin mass and process details in their production in many cases only by relatively minor differences or details.

Essentially, the laminate base production process consists in that a fibrous material web, especially a paper web provided with some printed decoration, is impregnated with a thermosettable resin, more preferably with a possibly modified melamine, formaldehyde and/or urea resin, and optionally directly afterwards or even later - optionally with the interposition of a possibly multilayer paper web likewise impregnated with a thermosettable resin - as a decorative laminate web with an abrasion-resistant surface layer is bonded to a substrate such as especially a wood chipboard or fiberboard under the action of heat and pressure. Currently, the technique predominates of subjecting the resin of the decorative laminate web and possibly present core layer web(s) in each case only to partial setting and of bonding the laminate that has been preset in this way under the action of heat and pressure by means of the resin that is then cured completely ultimately to the wood material substrate provided in each case.

As relates to the prior art in the field of producing decorative laminates with an abrasion-resistant surface coating without an overlay film, a large number of proposals have been advanced for this purpose and in part also implemented, which will be briefly, by no means even only approximately completely, discussed below.

Thus, e.g., DE 28 58 182 C2 discloses a decorative web for producing decorative boards with high abrasion-resistance in which there is a thin, abrasion-resistant coating that is located over the decoration and that contains an abrasion-resistant mineral and furthermore a binder for the latter, and the binder is to be compatible with the resin mass used and permeable to this resin.

The production of a decorative laminate can proceed, as follows from, e.g., DE 2 800 762, such that first an aqueous suspension of aluminum oxide particles stabilized with microcrystalline cellulose is applied to the unimpregnated decorative web, after which drying takes place. Then, impregnation with a melamine-formaldehyde resin solution is undertaken, and finally this decorative wear web is hot-pressed with a core web and the substrate board. In such a decorative web, however, the abrasion-resistant fine mineral particles are displaced by the microcrystalline cellulose to the outside or surface, the surface resin layer, and then in part protrude out of it and thus cause unwanted roughness of this surface, and, as is much more serious, increased wear of the sheets of the pressing tools used in the production of the laminates as a result of inevitable damage to the sheet surface. In addition, according to this document, it is necessary to apply the abrasion-resistant final coating in a separate procedure, which in any case increases production costs.

DE 195 08 797 C1, in a process for producing a decorative laminate paper, calls for a mixture to be produced from melamine resin, α-cellulose, corundum as the hardening material, additives and adjuvants as well as water and for it to be applied to the visible side of a decorative paper sheet that has already been impregnated with resin in the previous process step, but that has been dried to a residual moisture content of a few percent, after which drying takes place. This type of process is designed to yield the advantage that the corundum particles on their extreme tops and edges that may still be "protruding" out of the desired wear layer are to be covered with a continuous resin film, which, however, cannot be fully done in practice. The jacketing of the hard material particles desired there at their extreme points, however, was not achieved in practice, with which damage to the pressing sheets or plates in hot-pressing of decorative laminates could never be completely prevented.

US 3 135 643 A discloses a laminate production method according to which the decorative web is first impregnated with a resin suspension, and the latter is coated still wet with a dispersion comprising melamine resin, quartz, cellulose, cellulose derivatives and water. The complete jacketing of the particles of the abrasive substance with resin that is essential for protecting the pressing plates and belts cannot be ensured with this method either, as shown.

EP 472 036 A1 discloses a two-stage "wet-in-wet" process for producing abrasion-resistant decorative laminates, according to which it is provided that the decorative web itself in any case within the framework of the first impregnation with resin is impregnated with a melamine resin dispersion containing particles of abrasive material up to a percentage desired in each case. The disadvantage of this type of addition of particles of abrasive material directly onto and into the paper web of the decorative laminate is that within the decorative cover layer, the distribution of particles is not homogeneous, so that in this first production step, local stiffening occurs. In a second step, then the resin dispersion likewise containing the abrasive substances is applied. The aforementioned zones of stiffening of the decorative web as a result of penetration of abrasive particles into the latter then in any case disrupt the flexibility of the decorative web in the actual coating process.

Furthermore, EP 732 449 A1 should be mentioned, according to which abrasion-resistant laminates are obtained by a decorative paper sheet that is to be coated or a web of this type first being impregnated with resin, after which drying to certain residual moisture content values takes place, after which then a resin mass containing the particles of abrasive substance, cellulose, resin and additives is applied to the impregnation layer that has been partially dried in this way. The disadvantage of this coating method is that genuine bonding of the impregnation resin bodies to the surface coating resin bodies that contain the particles of abrasive substance, which bonds can be mechanically highly loaded, is not achieved.

The processes described in the two patents US 4,713,138 A and US 4,971,855 A for producing laminates with abrasion-resistant surface coatings are likewise subject to the disadvantages that are inevitable in all known one-step impregnation coatings with particles of abrasive material that are known to date. According to the technology described there, a mixture containing particles of abrasive material, cellulose and the respective resin is applied to the paper to be impregnated, without pretreatment. As a result of the wicking and absorption action of the decorative paper that is present "unimpregnated," as a result of its fiber inhomogeneities, nonuniform wicking rates at different locations on the paper surface occur, by which more particles of abrasive materials are sucked up and bonded wherever faster wicking occurs, and zones of higher surface coverage by these particles than in other areas of the surfaces and thus the aforementioned zonal stiffening occur. The ordered mutual alignment of the particles that otherwise occurs is also disrupted by the described wicking action, so that in zones of increased wicking action, for example, nests of particles form that significantly disrupt the homogeneity of the properties of the abrasion-resistant surface of the laminates.

Regarding the aforementioned US 4,713,138, it should furthermore be stated that the microcrystalline cellulose there has the purpose of producing a uniform distribution of particles of abrasive material in the surface resin layer, which leads, however, to corners or edges of the particles that are located near the outer surface of the surface layer protruding beyond it and thus being able to damage the surface of the pressing sheets. This US-A also discloses use of polyethylene wax as a surface-active component that increases slip.

Addition of certain polyethylene waxes as lubricants in resin compositions for producing laminates also follows from US 4,741,946 A; in any case the abrasion values according to EN 438 of laminates produced according to this US-A are in the region of 150 revolutions and in no case reach those values that high-quality floor laminates must reach and that are supposed to be roughly at least 10,000 revolutions.

US 4,449,137 A and US 4,567,087 A disclose a laminate in which finely dispersed polyethylene wax is incorporated in the vicinity of its surface or actually on its surface. The objective there is specifically that the wax "blooms" during hot-pressing, therefore migrates to the surface. This is achieved there in that the polyethylene wax is applied in its own working step and not as a component integrated into the impregnation and coating resin mass.

The use of polyethylene waxes in laminates, especially those with overlay paper, follows furthermore from US 4,139,671 A, in any case there being no particles of abrasive material there in the surface layer, and, moreover, with respect to the use of laminates there for bowling alleys a high sliding action being desirable, therefore exactly the opposite of those properties that a floor laminate must have.

Last but not least, a process developed by the applicant himself for producing highly abrasion-resistant decorative laminates according to EP 875 399 B1 should be mentioned; its significant feature consists in that a layer containing particles of abrasive material composed of a mixture or dispersion of a thermosettable resin is applied to a decorative web that has been impregnated with resin beforehand, and the component of the resin decisive for the properties of the decorative laminate is formed by use of at least one natural substance that contains polysaccharides. In practice, it has been shown that by using these natural substances in the resin mass in and of itself, certain improvements compared to the prior art can be achieved, especially with respect to the especially desirable protection of the pressing sheets and pressing belts, in that, however, sporadic damage to the surfaces of the pressing belts or pressing sheets cannot be completely eliminated even by the additives provided according to this EP-B1.

In spite of the host of known suggestions for problem-free production of laminates with a surface finished to be abrasion-resistant, there furthermore remains the challenge of developing a process for producing decorative laminates with abrasion-resistant surface finishing that have a high-quality surface coating that is in fact free of particles of abrasive material protruding out of the surface layer without a protective resin coating, so that the aforementioned unacceptable damage to the pressing sheets or pressing belts that disrupt production, and possibly even lead to production stoppages and in this way cause high costs by "protruding" particles of abrasive material is almost completely precluded.

In view of the difficulties in the production of overlay-free laminates that to date have not been resolved to a satisfactory degree under any circumstances, the object of the invention is to devise a decorative laminate or substrate body coated with the latter for the most varied applications, but especially for floor boards, panels and the like, which on the visible side that is used has a surface coating that meets high or extremely high requirements in its clarity and decorative reproduction quality and that can be controlled in its wear properties to the highest abrasion values. Nevertheless, both with respect to the products to be used and also the production process, especially relative to protection of the pressing sheets and belts that is as complete as possible, the production process is to be fault-proof and economical, and is to take place within the framework of production methods that have been proven in the past in practice, and is to be able to be implemented on existing systems without extensive re-arrangements and modifications at essentially the same production rates.

It was found in the course of thorough tests that specific incorporation of quite specific substance mixtures into the resin matrix that ultimately after curing is to contain the particles of hard material that ensure the surface wear resistance of the laminates leads to unexpectedly high-quality, optically particular laminates that have especially high service quality and wearing properties matched to the use that is desired in each case, with simultaneously optimum incorporation of particles of abrasive material. In this connection, not only do no possible adverse effects on the production process occur due to, for example, expected problems with respect to thermal stability of the adhesive and bonding properties under prolonged action of heat, and with respect to mold or press separation properties, but especially also not with respect to damage to pressing sheets and belts by particles of abrasive material that must be unconditionally prevented. Rather, a compact and cost-minimized manner of production is made possible that leads to decorative laminate products with permanently cracking-resistant, highly abrasion-resistant surface coatings, so-called "liquid overlay" coatings.

According to one aspect of the present invention, there is provided a decorative laminate with abrasion-resistant surface coating , the laminate having at least one decorative web layer of an outside fibrous material web and/or paper web on a visible side, and provided with a decoration, wherein the at least one decorative web layer is impregnated and coated in a one-step process with a thermoset synthetic mass, the thermoset synthetic mass being finished to be abrasion-resistant, wherein particles of at least one-abrasion resistant material are distributed in the thermoset synthetic mass, the thermoset synthetic resin mass being integral with the at least one decorative web layer and having a closed or smooth outer surface, and

wherein the thermoset synthetic mass comprises at least one thermosettable synthetic resin from the group of melamine resins, formaldehyde resins and urea resins;

a wax blend based on a polyethylene, polypropylene and/or polyamide polymer or copolymer, and at least one cross-linked polyvinyl pyrrolide; and

at least one further additive and/or one further adjuvant,

wherein particles of the at least one-abrasion resistant material in the thermoset synthetic mass are located only directly on or directly bordering the at least one decorative web layer, and wherein the particles of the at least one-abrasion resistant material are α-aluminum oxide and α-corundum and/or tungsten carbide, and a distribution or covering density of the particles of the at least one-abrasion resistant material located in the thermoset synthetic mass proceeds from having the distribution or covering density of between 80% and 95% directly on the visible side of the at least one decorative web layer and follows a negative gradient toward the outer surface thereof where the distribution or covering density drops to a value of zero, the outer surface having a thickness range of from 0.05 to 0.15 mm.

The simultaneous presence of wax(es) and polyvinyl pyrrolidone(s) in the impregnation and coating resin mass that leads to unexpected new laminate properties is critical to the invention. They are the result of the arrangement of the abrasion-resistant particles of hard material distributed in the surface and wear resin layer that could not be specifically achieved in the past such that the particles settle in the inherently very thin surface layer to the actual decorative web surface, collect and concentrate there and in the immediate vicinity thereof. Only the following simplified explanation of this unexpected phenomenon can be tentatively made: The particles of abrasive material that are present in relatively high concentrations in the impregnation coating mass as a result of the action of the compound of the wax blend and polyvinyl pyrrolidone in this mass essentially no longer develop buoyancy, they therefore do not float, and thus provision has been made as a result for their no longer protruding out of the surface layer or wear layer, therefore no longer above the boundary between the surface resin layer and air space, for which, as was the case in the past, even if the protruding areas, tops, or the like were covered with a thin film of this hardened resin mass, there was essentially no protection against displacement of this thin film in the production process, and when plates are used, rapid abrasion of this film occurs, so that exposure of tops, edges, corners or the like of the particles of abrasive material that often protrude only in the micron or submicron range occurs, which, in spite of these inherently small dimensions, causes uncontrolled damage that could only be eliminated with relatively high costs on the surfaces of the pressure sheets or pressing belts, and surfaces that cannot be cleaned.

What furthermore occurs, surprisingly enough, is the fact that in spite of one-step application and impregnation, the disruptive formation of local or zonal "nests" or "clumps" of abrasive materials that was described above within the framework of the explanation of the prior art, as a result of topographically different wicking properties of the decorative web that can ultimately lead to disruptive local stiffening thereof, can no longer be observed, which likewise should be attributed to a significant degree to the novel wax blend-PVP compound that has been incorporated or integrated into the resin mass.

For the sake of completeness at this point, it is mentioned that the use of polyvinyl pyrrolidone(s) (PVP) in resins for laminates for pedestrian surfaces, therefore for abrasion-resistant floorboards or the like, was not known in the past. US 5,496,387 A mentions such use of PVP only for resins as binders for abrasive material particles in grinding materials, and according to this document, the sedimentation rate of the particles will be reduced, therefore their settling to a substrate is prevented.

With respect to the wax blend in the compound, the ratio of polyethylene and/or polypropylene -- that is/are present in addition to other components and/or modifiers and/or additives or the like -- to polyamide can vary within wide limits of between 0.1 to 10 and 100 to 0.1. The ratio is advantageously in the range of between 50 to 100 and 100 to 50.

Within the framework of the invention, a laminate whose partially set resin impregnation and coating masses is formed, wherein the wax blend contains a micronized thermoplastic polymer based on ethylene.

It has been found that the compound and especially the wax blend in the compound in the resin mass in the laminates according to the invention leads to a completely new wood-like feel or touch that causes a feeling of warmth, when walking on it with bare feet, that is unknown in previously known laminate floors.

Polyamides in the compound that has been incorporated into the resin mass or in its wax components support not only the described new feel, but furthermore contribute to increased resistance of the coating, especially also with respect to the prevention of cracking.

Both the prevention of cracking that was not achieved with any overlay film-free surface coating to date and that can be achieved for the first time according to the invention and the novel concentration of particles of abrasive material that occurs directly on or in the vicinity of the decorative web surface, therefore in the depth of the surface or wear resin layer of the new laminates, should be essentially due to the new compound in the set mass of the impregnation and coating resin, the cross linked polyvinyl pyrrolidone used together with the wax play an important role. The one cross-linked polyvinyl pyrrolide has a molecular weight in a range of from 25,000 to 750,000, and preferably from 100,000 to 500,000. It is polymerized into the resin and as a result of keto-enol tautometry of the OH groups has an action that modifies the resin in the direction of long-term freedom from cracking and that greatly surpasses the action of the celluloses used to date with conventional molecular weight ranges.

According to another aspect of the present invention, there is provided a decorative laminate wherein the particles of the at least one-abrasion resistant material have a tabular form and comprise at least 40% of the thermoset synthetic mass, and preferably at least 80%, and the average grain size of the particles of the at least one-abrasion resistant material is in a range of from 10 to 100 μm, and especially from 10 to 50 μm.

With respect to the type of particles of abrasive material or hard material that is to be especially preferred for preventing the "floating" effect of the particles of abrasive material, the use of corundum particles or aluminum oxide particles is especially preferred.

One measure that unexpectedly supports the specific "settling effect" of the particles of abrasive material that has been desired for a long time and that has now been achieved according to the invention surprisingly consists in adding spherules of silicate material, especially glass, to the resin mass that contains the abrasive material, with diameters in a range of from 30 to 100 μm.

The action of the glass spherules can be explained, for example, by the fact that they ensure, so to speak, a thickness of the surface or wear layer resin film between one another that corresponds to their diameter, which means effective material coverage for the particles of abrasive material that as a result of using the above-described wax-PVP compound have the inherently unexpected tendency that is used anyway according to the invention to settle within the surface layer toward the decorative web, by which the above-explained protrusion of regions of particles of abrasive material that lie only in the micron range over the surface level of the surface layer is prevented.

In order both to ensure the absence of cracks in the finished laminates on the surface over long time intervals and to further support protection of the pressing sheets and belts in their production of laminates, the presence of internal flexibilizing agents that therefore influence the molecular structure within the resin mass, and/or external flexibilizing agents that influence the macroscopically detectable properties thereof, such as external flexibilizers, preferably sugar, and/or glycols, such as diethylene glycol, and/or internal flexibilizers, such as ε-caprolactam and/or p-toluene sulfonic acide amine, and/or cross-linking regulators, preferably dicyanodiamide, acetoguanamine, and/or benzoguanamine is advantageous.

In particular the sugars mentioned can play an important part within the impregnation and coating resin mass, specifically because they have 8 free OH groups per molecule that are heavily incorporated into the resulting combination of molecules when the laminating resin, such as, e.g., melamine resin, condenses, and can modify them in the direction in which a possible tendency to residual cracking that is exceptionally low anyway is extremely effectively suppressed.

According to another aspect of the present invention, there is provided a decorative laminate wherein the thermoset synthetic mass contains one or more resin modifiers and/or cross-linking regulators.

The p-toluene sulfonic acid amide furthermore forms an advantageous additional modifier for the condensation process in the formation of melamine resin, which can be attributed to its tautomer properties that lead to the fact that chain breaks occur within the framework of resin condensation over a long condensation period, and thus the formation of large molecular chains that, as has been found, cause and intensify cracking to a significant degree is greatly reduced.

The thermoset synthetic mass additionally contains at least one natural substance or substance identical to the at least one natural substance selected from the group of guar seed flour, flour(s) of Jerusalem artichoke, chicory and/or dahlia, locust bean gum flour, cesa gum, guar gum, gum arabic, carrageen, tragacanth gum, agar agar and/or xanthenes.

In the meaning of the aforementioned statements, with respect to preventing damage to the pressing sheets and belts of the production lines, on the one hand, and the prevention of cracking in new floor panels or laminates for floor panels in use, the natural substances can perform good additional support services.

A quantitative portion of the wax blend contained in the thermoset synthetic mass is 0.5 to 2.5% relative respectively to an entirety of the thermoset synthetic mass without the at least one-abrasion resistant material.

Further, a quantitative portion of the at least one cross-linked polyvinyl pyrrolide contained in the thermoset synthetic resin mass is 1.5 to 12% (and preferably 3% to 8%) relative respectively to an entirety of the thermoset synthetic mass without the at least one-abrasion resistant material.

A novel process for producing the new, cracking-free laminates finished to be abrasion-resistant relates to another important subject of the invention.

For a rough assessment, the range of quantitative contents of the primary and secondary components of the decorative web impregnation and wear layer coating resin masses for floor boards, preferably used within the framework of the invention, is mentioned below:

0.5 to 1% of silane(s),

2.0 to 4% of xanthene,

15 to 30%, especially 20 to 25%, of abrasive or hard material particles,

0.5 to 3% of polyvinyl pyrrolidone(s) (PVP)

0.2 to 1.5% of wax blend: polyethylene wax basis (e.g., from the PORO, Pointner und Rothschädl Company, Salzburg)

3 to 10% of sugar (saccharose)

0.3 to 1% of p-toluene sulfonic acid amide

0.1 to 0.5% of hardener

remainder to 100% of melamine resin (emulsion or solution)

By omitting the overlay film that reduced cracking in the past and presumably due to the composition that has been changed or modified by the new wax-blend-PVP compound in the resin masses, significant beneficial changes of a sensory type in walking barefoot on the new laminate arise when it is used for floors or floor boards: the sensory impression of the "cold" of the melamine resin surface that is typical for existing laminate floors known in the art no longer occurs in floors with the "liquid overlays" according to the invention that contain the above-described compound in the resin mass. The sensory impression of the floor on the user can be best paraphrased with the expression "warm underfoot." Until now, in most cases, carpets were generally laid on laminate floors with panels or boards produced using conventional technology, at least in the seating area, in order to prevent the aforementioned "cold" of known laminates from becoming noticeable.

When using the laminates according to the invention with the overlay-free surface or wear layer formed with the wax blend-PVP compound, it has therefore become possible for the first time to produce laminate floors that are warm underfoot according to EN 13329. By eliminating the overlay paper, a clear optical impression of the decoration of the new laminates that are intended especially for floors that had never been achieved in the past is attained. Essentially, in this invention, the effect that could not be achieved to date with any overlay-free laminate, that is, the effect of suppression of cracking that has been achieved in fact for the first time over the service life of the floor in the surface and wear resin layer, plays a quite important role.

Example:

The following production steps were carried out in succession, the initial materials used being explained below in detail:

The following brief operating instructions were used; the explanations of the product designations that appear here and internal abbreviated designations likewise follow farther below.

Add 2.5 L of silanes Z-6020 (silane) to a mixer half-filled with "Formulation 38" emulsion, stir at 300 rpm for 5 minutes, add 10 L of "Premix," add 10 L of xanthene solution, increase rpm to 500 rpm, mix in 50 kg of "ZWSK 220" corundum and 50 kg of "ZWSK 180" corundum, add 5 kg of polyvinyl pyrrolidone (PVP), admix 1.2 kg of wax blend, 600 ml of Vxt 3797 Hypersal as a wetting agent, 29 kg of granulated sugar, 3 kg of paratoluene sulfonic acid amide and 1.5 L of hardener H 806. Finally, add "Formulation 38" emulsion to make 420 L, reset rpm to 300 rpm, and mix completely within about 5 minutes. A pourable mass with a gelling time of 3 minutes and 40 seconds is obtained.

The application values of the described resin-abrasive particle mixture were 70 g/m^2 decorative paper with a final weight of roughly 210-220 g/m^2. The resulting resin-impregnated, surface-coated decorative web with abrasive particles applied was brought to a residual moisture content of from 6% to 6.5%. There would be a risk of agglutination of the resin film at a residual moisture content of more than 7%.

The decorative web obtained after partial setting was applied directly on a "Hymmen" unit at 37 m/minute of feed to floor panel boards made of fine fiber wood material and was hot-pressed at 240°C and a pressure of 20 bar.

More detailed explanations of the components of the resin impregnation and surface coating mass produced as just described follow:

"Premix" Production Instructions:

At 20°C in a Drais mixer, 4.5 kg of locust bean gum is stirred into 150 L of VE water at 500 rpm, and after the cooling system is turned off, the mixer rpm is increased to 900 rpm. The solution becomes more and more viscous after roughly 1.5 hours and heats up as a result of the friction heat generated by the rotor-stator stirring tool up to boiling. After roughly 1 hour of cooking time, the mixer rpm is reduced to 300 rpm, the cooling is turned on, 150 L of VE water is added, and within roughly 2 hours, cooling to roughly 40°C takes place. After adding 7.5 kg of hardener 528 (BASF) and a subsequent 10 minutes of mixing, then another 120 L of VE water is added, and finally cooling continues until 20°C is reached. The solution obtained in this way can be processed for up to roughly 1 week.

The "xanthene solution" that is used is a 1% solution of xanthene in water to which 0.3% formaldehyde is added to stabilize the solution.

The mixture according to "Formulation 38" is a melamine resin emulsion with 250 kg of 50% melamine resin, 4.8 kg of etherified melamine resin as the modifier, 0.4 kg of Alton MF 179 (WIZ Company, Italy) as the wetting and separating agent, 0.7 kg of Alton 1263 (WIZ Company, Italy) as a transparency enhancer, 0.3 kg of hardener 529 (BASF, Germany) and 2.0 kg of hardener 806 (KS Deurotex) based on diethanolamine.

"Silane Z 6020" (Dow Chemicals, USA) is an amino silane.

The "ZWSK corundum" used as the abrasive substance (Triebacher Company, Villach, Austria) bears this designation due to the special manner of its production, the attached numbers 220 and 180 designating the average grain size in μm.

This "wax blend" is produced as follows: The important components intended for this purpose, e.g., based on polyethylene and polyethylene derivative thermoplastics, or, generally speaking, polyalkylene or polyalkylene derivative thermoplastics, are cast into blocks, which are crushed after cooling, and starting with a certain size are ground or micronized in a jet mill. Each of the components is brought to the grain sizes desired in each case, e.g., by screening, classifying or the like, and in each case, e.g., two or more different grain size fractions of the different materials are mixed with one another in a corresponding ratio to one another. Screening characteristics and the component mixing ratios are known to the manufacturer.

The "Hypersal VXT 3797" (Solutia Company, Germany) used in the resin impregnation and coating mass is a commercial wetting agent.

The polyvinyl pyrrolidones (PVP) used here, generally called "cross-linked polyvinyl pyrrolidones" (BASF, Germany) have the commercial names "Luvicross" and "Luvicross M" and contain up to 6.0% of water, 11.0 to 12.8% of nitrogen, 0.5% of ash and less than 50 mg/kg of heavy metals. They are supplied in powder form. Their molecular weight can only be given as an order of magnitude.

The p-toluene sulfonic acid amide that can be used within the framework of the invention and the example is known as a chain stopper and can, as has been found, contribute to a certain extent to preventing the above-described, unwanted cracking in the overlay film-free laminate surface layer.

The tendency to cracking that could not be completely managed in the past and that has already been addressed several times can be further restrained especially effectively by the commercial sugar (saccharose) that is intended as the other component that can be more preferably used in the resin coating mass (also other disaccharides and oligosaccharides can be used).

The new floor laminates produced on the basis of the aforementioned data are characterized by highly wear-resistant surface films. They can be easily produced within conventional laminate pressing times and under the conditions that are otherwise common in laminate production.

Floor panels that have been hot pressed with a deep-structured decorative sheet based on the previous example show outstanding quality: the degree of closing of the surface and coating resin film is outstanding. In a "vapor test," no bubbles form and graying does not occur either. For curing in a drying oven at 70 and 100°C, even after 24 hours no cracks form, which is also the case at a still higher temperature, specifically at 120°C, likewise after 24 hours.

When testing the laminate surface by coloring it with graphite, an abrasive agent grain that penetrates the outer surface of the resin coating cannot be detected. The abrasion test yielded outstanding values of abrasion resistance up to the highest abrasion class, AC5 according to EN 13 29.

Last but not least, the completely unexpected touch or feel of the products according to the invention that is conspicuously pleasant compared to previously known laminate floors, specifically a new type of transfer of a feeling of warmth when walking barefoot on the floor prepared with panels produced using the new resin impregnation and coating mass that is comparable to roughly the feeling of walking on a waxed natural wood parquet floor should be especially emphasized.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A decorative laminate with abrasion-resistant surface coating , the laminate having at least one decorative web layer of an outside fibrous material web and/or paper web on a visible side, and provided with a decoration, wherein the at least one decorative web layer is impregnated and coated in a one-step process with a thermoset synthetic mass, the thermoset synthetic mass being finished to be abrasion-resistant, wherein particles of at least one-abrasion resistant material are distributed in the thermoset synthetic mass, the thermoset synthetic resin mass being integral with the at least one decorative web layer and having a closed or smooth outer surface; and

wherein the thermoset synthetic mass comprises at least one thermosettable synthetic resin from the group of melamine resins, formaldehyde resins and urea resins;

a wax blend based on a polyethylene, polypropylene and/or polyamide polymer or copolymer, and at least one cross-linked polyvinyl pyrrolide; and

at least one further additive and/or one further adjuvant;

wherein particles of the at least one-abrasion resistant material in the thermoset synthetic mass are located only directly on or directly bordering the at least one decorative web layer, and wherein the particles of the at least one-abrasion resistant material are α-aluminum oxide and α-corundum and/or tungsten carbide, and a distribution or covering density of the particles of the at least one-abrasion resistant material located in the thermoset synthetic mass proceeds from having the distribution or covering density of between 80% and 95% directly on the visible side of the at least one decorative web layer and follows a negative gradient toward the outer surface thereof where the distribution or covering density drops to a value of zero, the outer surface having a thickness range of from 0.05 to 0.15 mm.

2. The decorative laminate according to claim 1, wherein the wax blend contains a micronized thermoplastic polymer based on ethylene.

3. The decorative laminate according to claim 1 or 2, wherein the at least one cross-linked polyvinyl pyrrolide has a molecular weight in a range of from 25,000 to 750,000.

4. The decorative laminate according to claim 1 or 2, wherein the at least one cross-linked polyvinyl pyrrolide has a molecular weight in a range of from 100,000 to 500,000.

5. The decorative laminate according to any one of claims 1 to 3, wherein the particles of the at least one-abrasion resistant material have a tabular form and comprise at least 40% by weight of the thermoset synthetic mass, and the average grain size of the particles of the at least one-abrasion resistant material is in a range of from 10 to 100 μm.

6. The decorative laminate according to any one of claims 1 to 3, wherein the particles of the at least one-abrasion resistant material comprise at least 80% by weight of the thermoset synthetic mass and the average grain size of the particles of the at least one-abrasion resistant material is in a range of from 10 to 50 μm.

7. The decorative laminate according to any one of claims 1 to 4, wherein, in the at least one decorative web layer, in addition to the at least one-abrasion resistant material, there are spheroidal silicate spherules with diameters in a range of from 30 to 100 μm.

8. The decorative laminate according to claim 7, wherein the spheroidal silicate spherules are glass spherules.

9. The decorative laminate according to any one of claims 1 to 8, wherein the thermoset synthetic mass contains one or more resin modifiers and/or cross-linking regulators.

10. The decorative laminate according claim 9, wherein the thermoset synthetic mass contains one or more external flexibilizers and/or internal flexibilizers.

11. The decorative laminate according claim 10, wherein the thermoset synthetic mass contains sugar, a glycol, ε-caprolactam, p-toluene sulfonic acid amide, dicyanodiamide, acetoguanamine, and/or benzoguanamine.

12. The decorative laminate according claim 11, wherein the glycol is diethylene glycol.

13. The decorative laminate according to any one of claims 1 to 12, wherein the thermoset synthetic mass additionally contains at least one natural substance or substance identical to the at least one natural substance selected from the group of guar seed flour, flour(s) of Jerusalem artichoke, chicory and/or dahlia, locust bean gum flour, cesa gum, guar gum, gum arabic, carrageen, tragacanth gum, agar agar or xanthenes.

14. The decorative laminate according to claim 13, wherein the thermoset synthetic mass additionally contains locust bean gum flour and/or xanthenes.

15. The decorative laminate according to any one of claims 1 to 14, wherein a quantitative portion of the wax blend contained in the thermoset synthetic mass is 0.5 to 2.5% by weight relative respectively to an entirety of the thermoset synthetic mass without the at least one-abrasion resistant material.

16. The decorative laminate according to any one of claims 2 to 14, wherein a quantitative portion of the at least one cross-linked polyvinyl pyrrolide contained in the thermoset synthetic resin mass is 1.5 to 12% by weight relative respectively to an entirety of the thermoset synthetic mass without the at least one-abrasion resistant material.

17. The decorative laminate according to any one of claims 2 to 14, wherein a quantitative portion of the at least one cross-linked polyvinyl pyrrolide contained in the thermoset synthetic resin mass is 3 to 8% by weight relative respectively to an entirety of the thermoset synthetic mass without the at least one-abrasion resistant material.

18. A process for producing a decorative laminate as defined in claim 1, comprising impregnating and coating the at least one decorative web layer of the outside fibrous material web and/or paper web on the visible side in a one-step process with the thermoset synthetic mass thereby forming a closed or smooth outer surface.