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(54) Title: VARNISH COMPOSITIONS AND THEIR USE FOR THE COATING OF SURFACES OF SUBSTRATES

(57) Abstract: Varnish composition containing particles of calcium carbonate and their use for the coating the surfaces of various substrates. The resulting dried varnish compositions exhibit good surface aspect, good mechanical resistance, good matting effect and good resistance to liquid stain. The varnishes compositions can be used for exterior and interior applications.



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Varnish compositions and their use for the coating of surfaces of substrates

The invention relates to varnish compositions. More specifically, it relates to varnish compositions suitable for the coating of surfaces of substrates.

Varnishes confer to substrate surfaces onto which they are applied numerous properties like high mechanical resistance (to fissuring and scratch, for instance), high flatness, high heat resistance, low permeability to liquids (water, alcohols, etc.), low opacity (contrast ratio), good surface aspect and low gloss (matt effect), to mention only a few of them. The varnish compositions on the market at present day generally contain pyrogenic silica. Pyrogenic silica guarantees a good matting effect but it presents several drawbacks. It is a relatively expensive material. Pyrogenic silica is formed of fine particles and can lead to irritation of the respiratory tract if improperly handled (see for instance "Ullmann's Encyclopedia of Industrial Chemistry, Fifth, Completely Revised Edition, Volume A 23, Pages 635 to 942, Pyrogenic Silica"). And last but not least, pyrogenic silica can be difficult to disperse in aqueous media which are becoming the current basis for varnish compositions. There is therefore a need for new varnish compositions with less or without pyrogenic silica exhibiting similar or improved properties with respect to the current ones.

It is the aim of this invention to provide varnish compositions containing additives which are non toxic, cheaper and easier to handle than pyrogenic silica, and which confer to the surfaces of substrates onto which they are applied similar or improved, surface aspect (low opacity), superficial hardness, gloss, and liquid stain resistance, with respect to varnish compositions of the prior art.

The invention relates then to varnish compositions containing particles of calcium carbonate.

It has surprisingly been found that when in varnish compositions, pyrogenic silica is at least partially replaced by particles of calcium carbonate, good surface aspect (low opacity), good superficial hardness, acceptable gloss and good liquid stain resistance are obtained for the substrate surfaces onto which the varnish have been applied. The varnish compositions containing the particles of calcium carbonate can be used for exterior and interior applications.

By varnish compositions one intends to denote varnishes ready to use or any premix of components which can be incorporated into varnishes before they

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are ready to use. Examples of such premixes are mixtures containing a binder, a solvent and at least one component selected from antifoaming agents, water emulsion waxes, antifreeze coalescent agent and wetting agents.

Varnish compositions (referred hereafter equally to varnishes) are liquid, paste or powder products which can be applied to surfaces of various substrates by various methods and equipment in layers of given thickness. These form adherent films on the surface of the substrate, the film formation occurring by drying. The drying takes place physically or chemically depending on the varnish compositions. Evaporation of solvents and cooling of the melted powder are examples of physical drying. Chemical drying takes place by chemical reaction between varnish components and involves for instance, polymerization and cross-linking reactions. Unlike paints, the films formed on the surface of the varnished substrates are transparent. The transparency or its opposite the opacity of the film can be measured according to standard UNI ISO 3905-1990. For varnishes, the opacity of the film is lower than or equal to 10 %, preferably lower than or equal to 5 % and most preferably lower than or equal to 1 %, while for paints, the opacity is higher than or equal to 90 %, preferably higher than or equal to 95 % and most preferably higher than or equal to 99 %.

The varnish compositions of the invention are preferably liquid or paste products.

Varnishes can generally contain volatile and non-volatile components.

Volatile components are, for example, solvents and coalescing agents.

Solvents can be organic solvents or inorganic solvents or mixture thereof.

Inorganic solvents and mixtures of inorganic solvents and organic solvents are preferred.

Water is the preferred inorganic solvent.

Mixtures of water and at least one organic solvent are the preferred mixtures of inorganic and organic solvents. For such mixtures, the water content of the mixture is generally higher than or equal to 50 % by weight, preferably higher than or equal to 90 %, more preferably higher than or equal to 95 % and most preferably higher than or equal to 99 %. The organic solvent can be selected from alcohols, glycol ethers and oxygen-containing solvents that are soluble or miscible with water.

Varnish compositions where the solvent is only water or is a mixture of water and of at least one organic solvent have several advantages over varnishes containing only organic solvents : the main solvent is water, no environmentally

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polluting cleavage products are liberated during drying, fastness of the coating is excellent, water is noncombustible and non toxic.

5 The solvent content of the varnish composition is usually higher than or equal to 10 % by weight of the total varnish composition (volatile plus non volatile components), preferably higher than or equal to 25 % by weight and most preferably higher than or equal to 40 % by weight. In addition, the solvent content is generally lower than or equal to 80 % by weight of the total varnish composition, preferably lower than or equal to 70 % by weight and most preferably lower than or equal to 60 % by weight.

10 Coalescing agents are compounds that can be added to varnishes in order to help varnish coalescence and uniform film formation. Coalescing agents can be selected from different families of compounds like polyols and esters. Polyols are preferred. The content of the coalescing agent in the varnish composition is usually higher than or equal to 0.1 % by weight of the total
15 varnish composition, preferably higher than or equal to 0.5 % by weight and most preferably higher than or equal to 1.0 % by weight. The content of the coalescing agent is generally lower than or equal to 5 % by weight of the total varnish composition, preferably lower than or equal to 3 % by weight and most preferably lower than or equal to 2 % by weight.

20 As non-volatile components, varnishes may usually contain binders and other non-volatile components. Unlike paints, the varnishes of the invention usually do not contain neither pigments nor extender pigments as non-volatile components.

25 Binders usually contain film-forming substances, plasticizers and rheological modifiers.

Film-forming substances comprise generally macromolecular products with a molecular mass between 500 and ca. 30 000. The high molecular mass products can include among others, cellulose nitrate and vinyl chloride copolymers, which are suitable for film formation by physical drying. The low
30 molecular mass products can include alkyd resins, phenolic resins, polyisocyanates, and epoxy resins, which must be chemically dried after application to the substrate to produce acceptable films.

Most of the film-forming substances are resins, vitreous-amorphous solids without a defined melting point. Resins can be soluble in organic solvents or in
35 water. Resins which are soluble or easily dispersed in water are preferred. Aqueous dispersions of resins are more preferred.

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Water-soluble resins can be selected from low molecular mass polymers (lower than 10 000) e.g. alkyds, polyesters, acrylics, polyacrylates, epoxides, epoxy esters and polyurethanes. Polyurethane polymers, acrylic polymers, and mixtures thereof (polyurethane-acrylic polymers) are preferred.

- 5 Resins for aqueous binder dispersions can be selected from high molecular mass polymers e.g. of styrene, butadiene, acrylate, or vinyl monomers and mixtures thereof. Polyurethane-acrylic polymers are preferred. Such aqueous suspensions are sometimes referred to latex.

- 10 The content of the binder in the varnish composition is usually higher than or equal to 10 % by weight of the total varnish composition, preferably higher than or equal to 30 % by weight and most preferably higher than or equal to 50 % by weight. In addition, the content of the binder is generally lower than or equal to 90 % by weight of the total varnish composition, preferably lower than or equal to 80 % by weight and most preferably lower than or equal to 70 % by weight.

15 Plasticizers are generally organic liquids of high viscosity and low volatility. They can lower the softening and film-forming temperatures of the binders, improve flow, flexibility, and adhesion properties. Esters of polyacids (e.g. dioctyl phthalate) are typical examples.

- 20 Rheological modifiers can be selected from cellulose, bentonite, xantam gum derivatives and the so called associative thickeners, because they act directly onto the binder surface in order to create a network. Polyurethane associative thickeners are preferred.

- 25 The content of the rheological modifier in the varnish composition is usually higher than or equal to 0.1 % by weight of the total varnish composition, preferably higher than or equal to 0.5 % by weight and most preferably higher than or equal to 1.0 % by weight. In addition, the content of the rheological modifier is generally lower than or equal to 5 % by weight of the total varnish composition, preferably lower than or equal to 3 % by weight and most preferably lower than or equal to 2 % by weight.

- 30 Pigments and extenders are responsible for the color and the covering power of paints. They are finely ground crystalline solids that are dispersed in the paint. They constitute a major component of the paint and are usually present in an amount higher than 50 % by weight. The varnish composition of the invention may contain pigments. The amount of pigments is usually lower than or equal to 5 % by weight of the total varnish composition weight,

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preferably lower than or equal to 3 and most preferably lower than or equal to 1.5. Varnish compositions without pigments and pigment extenders are particularly well suited.

Other non volatile components that can be present in the varnish composition are usually used in small amounts to improve technical properties of the varnish. Examples are leveling agents, film-formation promoters, wetting agents, dispersants and anti-settling agents, antifoaming agents, antifreeze coalescent agent, catalysts, antifoaming and antiflooding agents, antiskinning agent, matting agents other than calcium carbonate, neutralizing agents, light stabilizing agents, thickening agents, preservatives and corrosion inhibitors, water emulsion waxes or dyes. Antifoaming agents, water emulsion waxes, antifreeze coalescent agent, wetting agent, and mixtures thereof are preferred.

The invention also relates to a varnish composition containing particles of calcium carbonate and at least one component selected from resins, antifoaming agents, water emulsion waxes, antifreeze coalescent agents, wetting agents and rheology modifiers.

The particles of calcium carbonate contained in the varnish of the invention can be particles of natural or synthetic calcium carbonate.

Natural calcium carbonate can be processed by mechanically crushing and grading calcareous ore to obtain particles adjusted to the desired size and surface area. Synthetic calcium carbonate is usually prepared by precipitation using various sources of calcium and carbonates ions. Synthetic calcium carbonate is preferred, especially precipitated calcium carbonate (PCC).

Particles of PCC may be manufactured by first preparing a calcium oxide (quick lime) by subjecting limestone to calcination by burning a fuel, such as coke, a petroleum fuel (such as heavy or light oil), natural gas, petroleum gas (LPG) or the like, and then reacting the calcium oxide with water to produce a calcium hydroxide slurry (milk or lime), and reacting the calcium hydroxide slurry with carbon dioxide to obtain the desired particle size and shape PCC (carbonation process). Carbon dioxide can be discharged from a calcination furnace for obtaining the calcium oxide from limestone, from gases from power plants or from liquid CO₂ containers for instance. It is preferred to use carbon dioxide discharged from a calcination furnace for obtaining the calcium oxide from limestone. Precipitation of calcium carbonate can also be carried out by adding an alkali metal carbonate starting with lime water (caustification method) or by the addition of an alkali metal carbonate starting with solutions containing

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calcium chloride. PCC particles obtained from the carbonation process are preferred.

The calcium carbonate can be substantially amorphous or substantially crystalline. Substantially amorphous or crystalline is understood to mean that
5 more than 50 % by weight, especially more than 75 % by weight, more particularly more than 90 % by weight of the calcium carbonate is in the form of amorphous or crystalline material when analyzed by an X-ray diffraction technique. Substantially crystalline calcium carbonate is preferred. Crystalline calcium carbonate can consist of calcite or aragonite or a mixture of these two
10 crystalline phases. The calcite phase is preferred.

In the case where the calcium carbonate is synthetic calcium carbonate, the primary particles can be of any shape. They may have the form of needles, scalenohedrons, rhombohedrons, spheres, platelets or prisms. A rhombohedral shape, that can be reduced to pseudo-cubes or pseudo-spheres, is preferred. The
15 primary particles are defined as the smallest individual crystallites. The shape of the primary particles can be obtained from Electron Microscopy analysis.

The calcium carbonate can also exhibit various nanoscale structures - hollow spheres, nano-fibers, nano-faggots, nano-rosaries, nano-platelets and nano-accordions. Such nano-scale structures are preferred. Nano-fagots are
20 particularly preferred nanoscale structures.

Hollow spheres are defined as hollow aggregates of primary particles having a mean primary particle size of less than 100 nm measured according to the standard NFX 11 601-1979/NFX 11 602-1977. They can be obtained by spray-drying of coated PCC suspensions.

25 Nano-fibers, nano-faggots, nano-rosaries, nano-platelets and nano-accordions are structures such as those obtained by means of the method described and claimed in patent application WO 03/004414 of SOLVAY (Société Anonyme). The definitions of nano-fibers, nano-faggots, nano-rosaries, nanoplatelets and nano-accordions are given in document WO 03/004414 of
30 SOLVAY (Société Anonyme), page 5, line 33 to page 7, line 9 and are incorporated herein by reference.

The calcium carbonate particles used in the invention have usually a BET specific surface area higher than 10 m²/g, preferably higher than or equal to 15 m²/g, more preferably higher than or equal to 25 m²/g, yet more preferably
35 higher than or equal to 50 m²/g, still more preferably higher than or equal to 75 m²/g and most preferably higher than or equal to 100 m²/g. The particles

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according to the invention have generally a BET specific surface area lower than or equal to 300 m²/g preferably lower than or equal to 250 m²/g, more preferably lower than or equal to 200 m²/g, still more preferably lower than or equal to 150 m²/g and in particular lower than or equal to 130 m²/g. The BET specific surface area is measured according to the standard ISO 9277-1995.

The calcium carbonate particles have usually a mean primary particle size (d_p) higher than or equal to 5 nm, preferably higher than or equal to 10 nm, more preferably higher than or equal to 30 nm, still more preferably higher than or equal to 50 nm and most preferably higher than or equal to 70 nm. The mean primary particle size is generally lower than or equal to 20 μ m, preferably lower than or equal to 10 μ m, more preferably lower than or equal to 1 μ m and most preferably lower than or equal to 0.1 μ m. The mean primary particle size is measured according to the standard NFX 11 601-1979/NFX 11 602-1977.

The calcium carbonate particles used in the invention can be coated with at least one coating agent. The coating agent can be selected from carboxylic acids, carboxylic acid salts, polyacrylic acids, polyacrylic acid salts and mixtures thereof.

The carboxylic acid may be aliphatic or aromatic. Aliphatic carboxylic acids are preferred.

The aliphatic carboxylic acid may be any linear or branched or cyclic, substituted or non substituted, saturated or unsaturated, aliphatic carboxylic acid. The aliphatic carboxylic acid has usually a number of carbon atoms greater than or equal to 4, preferably greater than or equal to 8, more preferably greater than or equal to 10 and most preferably greater than or equal to 14. The aliphatic carboxylic acid has generally a number of carbon atoms lower than or equal to 32, preferably lower than or equal to 28, more preferably lower than or equal to 24 and most preferably lower than or equal to 22.

The aliphatic carboxylic acid can be selected from the group of substituted, non substituted, saturated and unsaturated fatty acids or mixtures thereof. More preferably it is selected from the group consisting of caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, iso-stearic acid, hydroxystearic acid, arachidic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, melissic acid, myristoleic acid, palmitoleic acid, petroselinic acid, petroselaidic acid, oleic acid, elaidic acid, linoleic acid, linolelaidic acid, linolenic acid, linolenelaidic acid, α -eleostearic acid, β -eleostearic acid, gadoleic acid, arachidonic acid, erucic acid, brassidic acid and clupanodonic acid,

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mixtures thereof or salts derived therefrom. Mixtures containing mainly palmitic, stearic and oleic acids are more preferred. Mixtures called "stearine" which consist of about 30 – 40 wt % stearic acid, of about 40 - 50 wt % palmitic acid and of about 13 - 20 wt % oleic acid are particularly preferred.

- 5 The aliphatic carboxylic acid can be a rosin acid selected from the group consisting of levopimaric acid, neoabietic acid, palustric acid, abietic acid, dehydroabietic acid, mixtures thereof or salts derived therefrom.

10 In case that the coating agent is a salt of an aliphatic carboxylic acid, this may be the calcium salt of the carboxylic acid. However, the coating agent may also be present e.g. in form of the sodium, potassium or ammonium salt of the aliphatic carboxylic acid.

15 The coating agent may be applied to the particles by any suitable method. For instance, the coating agent can be dispersed or emulsified in liquid or solid form, preferably as an emulsion with the dispersed calcium carbonate, for example, during the grinding process or during and/or after the precipitation, the coating agent adhering to the surface of the calcium carbonate.

20 Preferably, the treatment of the alkaline earth metal carbonate with the coating agent takes place in emulsified form in an aqueous system. For further details, it can be referred to e.g. US 6,342,100 of SOLVAY SODA DEUTSCHLAND GmbH with is fully incorporated by reference herein.

25 The calcium carbonate particles can be coated with a polyacrylic acid, a polyacrylic acid salt or with a mixture thereof. The molecular weight of the polyacrylic acid is generally higher than or equal to 500 g/mol, preferably higher than or equal to 700 g/mol and most preferably higher than or equal to 1 000 g/mol. That molecular weight is usually lower than or equal to 15 000 g/mol, ideally lower than or equal to 4 000 g/mol and in particular lower than or equal to 2 000 g/mol.

30 In case that the coating agent is a salt of a polyacrylic acid, this may be the calcium salt of the polyacrylic acid. However, the coating agent may also be present e.g. in form of the sodium, potassium or ammonium salt of the polyacrylic acid. The sodium salt is preferred.

35 In case that the coating agent is a salt of a polyacrylic acid, it may be the crystallization controller as defined in document WO 03/004414 of SOLVAY (Société Anonyme), page 2, lines 24 to 31 which is incorporated herein by reference.

Preferably, the calcium carbonate particles used in the invention are coated with a coating the content of which being usually higher than or equal to 0.0001 wt %, preferably higher than or equal to 0.001 wt %, yet preferably higher than or equal to 0.01 wt % and most preferably higher than or equal to 0.05 wt %, based on the total weight of the particles. The coating content of the particles according to the invention is generally lower than or equal to 60 wt %, preferably lower than or equal to 25 wt %, yet preferably lower than or equal to 10 wt % and most preferably lower than or equal to 6 wt %, based on the total weight of the particles.

The calcium carbonate particles content of the varnish composition according to the invention is generally higher than or equal to 0.1 wt % of the total varnish composition, preferably higher than or equal to 0.5 wt % and most preferably higher than or equal to 1.0 wt %. That amount is usually lower than or equal to 10 wt % of the total varnish composition, preferably lower than or equal to 5 wt % and most preferably lower than or equal to 2 wt %.

The varnish compositions of the invention can be applied to surfaces of various substrates. The invention is therefore also related to the use of varnish compositions containing particles of calcium carbonate for the coating of substrates which can be selected from metals, wood, wood-based materials, cardboard, paper, elastomers, rubbers, plastic, glass, ceramics, concrete, mortar, cement render, gypsum, bricks, stone, composite materials, synthetic and natural leather, and keratinic materials. Wood and wood-based materials are preferred substrates.

Wood is a natural raw material which consists of a framework of cellulose, together with lignin and hemicellulose.

Wood-based materials are materials obtained from the combination of small pieces of wood with a suitable binder. Plywood, chipboard and multilayer wood are preferred wood-based materials.

The varnishes compositions of the invention can be applied to surfaces of various substrates as primers, intermediate coats and topcoat. By primer, one intends to denote the first layer applied to the surface. It is generally used to fill the porosity of the material if any and/or to improve the compatibility of the substrate surface with the next layers. By topcoat, one intends to denote the outer layer of varnish to be coated on the substrate. It is preferred to use the varnishes of the invention as topcoats, more preferably as topcoat for wood substrates.

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The varnish composition according to the invention can be used for the preparation of wood topcoatings for coating furnitures, fixtures, parquet floor, etc. The coating can have a thickness from 0.01 mm to 0.1 mm. It can be applied by any technique usually used in the protection industry : by brush, by
5 roller, by spray-gun, etc. After the application, the time to assess the complete physico-chemical transformations necessary to transform the varnish liquid film into a solid one is usually called drying time.

The superficial hardness of the varnish composition of the invention after drying is measured according to the standardized test EN ISO 1522-2001 (Konig
10 pendulum test). The varnish composition is applied and dried on a glass surface (200 μ m wet thickness), then the hardness measurement is related to the pendulum-oscillation-time. The higher is this time (express in seconds), the higher is the superficial hardness of the film. The oscillation time is usually higher than or equal to 10 s, preferably higher than or equal to 50 s and most
15 preferably higher than or equal to 100 s. That time is usually lower than or equal to 250 s, preferably lower than or equal to 200 s and most preferably lower than or equal to 150 s.

The alteration of the surface aspect of the wood support is related to the opacity of the varnish composition after drying and is measured according to the
20 following procedure. The product is applied and dried on a white/black paper support (200 μ m wet thickness) and then the % opacity (contrast ratio) is determined by a spectrophotometric instrument X-Rite SP64. The opacity of the film is usually lower than or equal to 50 %, preferably lower than or equal to 30 % and most preferably lower than or equal to 10 %.

25 The matting effect of the varnish composition of the invention after drying), is obtained from the reflectometric measurements of gloss-grade of the film, according to a method based on the standardized test UNI EN ISO 2813-2001. The gloss measurements are not done using a dark glass support but by applying the varnish on a dark paper support. Moreover, the
30 film applications are performed using a 200 μ m wet film applier instead of a 150 μ m one as indicated in the standardized test. The gloss of the film is usually lower than or equal to 70 %, preferably lower than or equal to 50 % and most preferably lower than or equal to 30 %.

The resistance to liquid stain of the varnish composition of the invention
35 after drying, is measured according to the standardized test

UNI EN ISO 2812-1-1996 (method n° 2). The testing liquids are : water (tap water,), ethyl alcohol, Coca-Cola® (normal) and coffee (commercial expresso).

The following examples further illustrate the invention but are not to be construed as limiting its scope.

5 Example 1 (according to the invention)

Nano-faggots of precipitated calcium carbonate have been obtained according to the procedure described in example 5 of patent application WO 03004414 of SOLVAY (Société Anonyme). After drying, 11.00 g the product have been dispersed in 89 g of water.

10 Exemples 2 to 6 (according to the invention)

Other PCC particles have been obtained according to the procedure described in example 3 of patent application WO 03004414 of SOLVAY (Société Anonyme). The slurry obtained (11 % w/w of PCC in water) is ready to use.

15 The characteristics of the various PCC are summarized in Table 1.

Examples 7 (not according to the invention)

12.70 g of silica TS-100 from Degussa have been dispersed in 86.3 g of water.

20 Examples 8 to 25 (according to the invention) and Examples 26 to 28 (not according to the invention)

Varnish compositions have been prepared as follows : 71.241 g of a resin (SANCURE AU-4010 from Noveon) and 0.389 g of an anti-foaming agent (BYK 028 from Byk-Chemie) have first been mixed together at 200 rpm, at room temperature and for 10 min in a Dispermat by Vma-Oetzmman mixing device. 2.433 g of a water emulsion wax (ULTRALUBE D-819 from Ashland), 1.752 g of a water emulsion wax (AQUACER-513 from Byk-Cera), the amounts of water and of the dispersions of examples 1 to 7 indicated in Table 2, 1.744 g of an antifreeze-coalescent agent (DOWANOL DpNB from Dow Chemical), 0.986 g of a wetting agent (TROYSOL LAC from Troy) and 0.682 g of a rheology modifier (NOPCO DSX-1514 from Cognis) have then been added and the resulting mixture has been mixed at 800 rpm, at room temperature for 30 to 40 min.

Example 29 (not according to the invention)

35 A varnish composition has been prepared according to procedure described for the examples 8 to 28 excepted that no water and none of the dispersions of examples 1 to 7 have been added.

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Table 2 gathers the various compositions.

The results of the various tests performed on the dried varnish compositions are reported in Table 3

Table 1

Example	Surface area (m ² /g)	Nano-structure
1	24	Nano-faggots
2	67	none
3	99	none
4	121	none
5	73	none
6	125	none

5 Table 2

Varnish composition example N°	PCC or silica dispersion example N°	PCC or silica dispersion (g)	Water (g)
8	1	10.387	10.387
9	1	15.58	5.193
10	1	20.773	0
11	2	10.387	10.387
12	2	15.58	5.193
13	2	20.773	0
14	3	10.387	10.387
15	3	15.58	5.193
16	3	20.773	0
17	4	10.387	10.387
18	4	15.58	5.193
19	4	20.773	0
20	5	10.387	10.387
21	5	15.58	5.193
22	5	20.773	0
23	6	10.387	10.387
24	6	15.58	5.193
25	6	20.773	0
26	7	9.00	11.76
27	7	13.5	7.274
28	7	17.976	2.797
29	-	0	0

Table 3

Varnish composition	GLOSS (60°)	OPA-CITY ¹ (%)	SUPER-FICIAL HARDNESS ² (seconds)	LIQUID STAIN RESISTANCE											
				PLYWOOD				CHIPBOARD				MULTILAYER WOOD			
				WATER	ALCO-HOL	COKE	COF-FEE	WATER	ALCO-HOL	COKE	COF-FEE	WATER	ALCO-HOL	COKE	COF-FEE
8	40,7	7,3	121,8	NO	NO	NO	NO	YES	NO	YES	NO	NO	NO	NO	NO
9	39,5	7,3	123,0												
10	36,9	7,4	125,4												
11	43,6	7,3	117,5	NO	NO	NO	NO*	YES	NO	YES	YES	NO	NO	NO	NO
12	37,8	7,3	122,2												
13	32,8	7,2	125,5												
14	45,7	7,3	117,4	NO	NO	NO	YES	YES	NO	YES	YES	YES	NO	NO	NO
15	43,1	7,4	114,2												
16	39,0	7,4	123,6												
17	41,9	7,4	120,0	NO	NO	NO	NO	NO	YES	NO	YES	NO	NO*	NO	NO
18	39,3	7,4	126,4												
19	35,5	7,3	127,6												
20	28,4	7,2	123,6	NO	NO	NO	NO*	NO	NO	NO	NO*	YES	NO	NO	NO
21	21,1	7,3	123,0												
22	16,3	7,3	127,4												
23	38,9	7,3	125,4	NO	NO	NO	NO	YES	YES	NO	NO	NO	NO	NO	NO
24	32,0	7,2	122,6												
25	27,8	7,2	127,8												
26	17,4	7,3	112,8	NO	NO	NO	NO	NO	NO	YES	NO	NO	NO	NO	NO
27	12,6	7,4	114,8												
28	9,4	7,4	103,0												
29	56,5	7,3	116,0												

1. Opacity is related to the contrast ratio measurement

2. Superficial Hardness : test results after 30 days of drying

3. YES = no stain, NO = evident stain, NO* = light stain

CLAIMS

1. Varnish composition containing particles of calcium carbonate.
2. Varnish composition according to claim 1 containing in addition at least one solvent.
- 5 3. Varnish composition according to claim 2, wherein the solvent is water and the water content of the varnish composition is higher than or equal to 10 % by weight and lower than or equal to 80 % by weight.
4. Varnish composition according to any of claims 1 to 3 wherein the calcium carbonate particles have a BET specific surface area higher than or equal
10 to 10 m²/g.
5. Varnish composition according to any of claims 1 to 4 wherein the calcium carbonate is precipitated calcium carbonate.
6. Varnish composition according to claim 5 wherein the precipitated calcium carbonate particles exhibit a nanometric scale structure selected from
15 nano-fibers, nano-faggots, nano-rosaries, nanoplatelets and nano-accordions.
7. Varnish composition according to any of claims 1 to 6 wherein the calcium carbonate particles are coated with at least one coating agent selected from fatty acids, fatty acid salts, polyacrylic acids and polyacrylic acid salts.
8. Varnish composition according to any of claims 1 to 7 containing in
20 addition at least one component selected from resins, antifoaming agents, water emulsion waxes, antifreeze coalescent agents, wetting agents and rheology modifiers.
9. Varnish composition according to any of claims 1 to 8 wherein the calcium carbonate particles are incorporated in an amount higher than or equal to
25 0.1 wt % and lower than or equal to 10 wt % with respect to the total weight of the varnish composition.
10. Use of calcium carbonate particles in the varnish compositions of any one of claims 2 to 9.

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11. Use of the varnish composition of any of claims 1 to 9 for the coating of surfaces of substrates selected from metals, wood, wood-based materials, cardboard, paper, elastomers, rubbers, plastic, glass, ceramics, concrete, mortar, cement render, gypsum, bricks, stone, composite materials, synthetic and natural
5 leather, and keratinic materials, preferably from wood and wood-based materials.