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(54) Title: HYBRID POLYMER COATING FOR PETROUS OR CERAMIC SUBSTRATES, PETROUS OR CERAMIC SUBSTRATE, AND OBTAINING METHOD

(57) Abrégé/Abstract:
A coating having a thickness between 0.1 and 2 mm is obtained from a mixture with the following composition: 10-25% by weight of micronized powder; 40-60% by weight of inorganic gravels of petrographic origin of sizes comprised between 0.063 - 2 mm; 10-40% by weight of a polymerisable base resin selected from polyurethane, polyester, epoxy or acrylic, with additives; and optionally pigments. The proportion of the mentioned gravel and micronized powder of the coating is up to 90% in an inner most area of interphase between coating and surface of the petrous substrate, covering one third of the thickness of the coating. The method comprises depositing the mentioned mixture on the substrate and vibrating the assembly, and subsequently proceeding to a step of curing and subsequent mechanical finishing of the surface.

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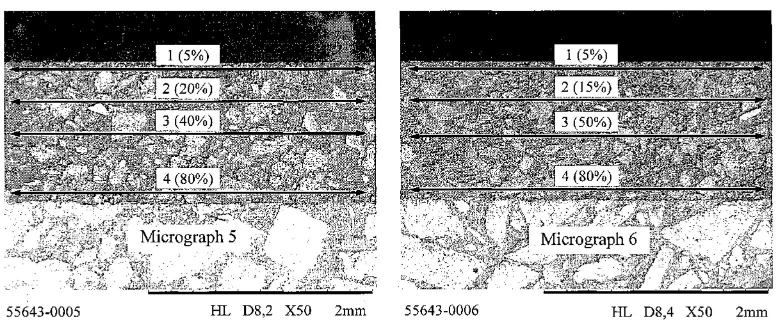

Fig. 1

(57) Abstract: A coating having a thickness between 0.1 and 2 mm is obtained from a mixture with the following composition: 10-25% by weight of micronized powder; 40-60% by weight of inorganic gravels of petrographic origin of sizes comprised between 0.063 - 2 mm; 10-40% by weight of a polymerisable base resin selected from polyurethane, polyester, epoxy or acrylic, with additives; and optionally pigments. The proportion of the mentioned gravel and micronized powder of the coating is up to 90% in an inner most area of interphase between coating and surface of the petrous substrate, covering one third of the thickness of the coating. The method comprises depositing the mentioned mixture on the substrate and vibrating the assembly, and subsequently proceeding to a step of curing and subsequent mechanical finishing of the surface.

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HYBRID POLYMER COATING FOR PETROUS OR CERAMIC SUBSTRATES, PETROUS OR CERAMIC SUBSTRATE, AND OBTAINING METHOD

The present invention relates, in a first aspect, to a coating which provides a very thin layer (thickness being at most of the order of 2 mm and generally considerably less) applicable to natural or artificial petrous substrates, particularly to marble agglomerate, as well as to ceramic substrates on which the coating is firmly adhered to.

The surfaces of marble agglomerate comprise calcareous mineral loads having as main drawbacks a low resistance to scratching and poor chemical resistance against acids. These properties are determined by the mineral used as load which on the other hand, since the marble is not very abrasive, provides the advantage of being able to use a manufacturing process with high productivity if compared with the manufacturing of quartz boards and tiles.

The proposed coating provides a hardness and resistance to chemical attack comparable to quartz, allowing using substrates of reduced thickness of the order of 6 to 12 mm, being able to use materials recycled from the natural stone cutting production process for the constitution of said substrate as well as the coating, increasing the recyclable material content of the petrous agglomerate and of the coating.

In a second aspect the invention refers to a petrous or ceramic substrate provided with a hybrid polymer coating according to the principles of this invention.

Lastly, the invention also refers to a method for obtaining the mentioned hybrid polymer coating which is carried out on a petrous or ceramic substrate and which renders a product protected by said coating.

Background of the Invention

EP 790222 describes a stone agglomerate comprising a first component with fine inorganic particles and a second component with micro-particles, wherein said fine particles or aggregates thereof are transparent and are coated by a layer of inorganic or organic material having a thickness comprised between 5 and 50 microns such that said layer is partially fragmented and exposes the component on the surface producing an accentuated reflection of the light.

Patent US 4640850 describes a composite slab incorporating a sheet of marble or petrous coated on its visible face by a sheet of transparent glass. This patent refers to the preceding patent US 4177789 describing a method for obtaining marble boards having thicknesses less than 10 mm and generally up to 4 mm, which are reinforced on their not visible face by means of a glass fiber covering, indicating that the visible face of the slab is provided with some type of reinforcement. EP 799949 describes a thin natural stone element joined by a transparent polyester resin to a glass plate support. EP 1375130 describes a composite slab with a multilayered coating based on overlapping glass plates.

Patent WO 0114133 describes a method for obtaining a multilayer composite slab with a sandwich type structure with an intermediate layer of expanded light material comprised between an upper layer of stone agglomerate obtained by mixing crushed stone, powder and a binder in required proportions, introducing the mixture in a mold and performing a process of vibro compression in said mold and optionally a lower layer of agglomerate with similar characteristics.

Patent JP 11138703 describes a multilayer material for laminating having flexion and impact high performances and incorporating a visible surface of wood agglomerate, calcium carbonate, hollow crystal balls, talc, etc., comprising flexible middle support layers.

Patent FR 2868099 describes a decorative panel for panels or ceilings with a multi-layer surface of a thermoplastic composite with load mineral, fibers or other particles attached to an extruded polystyrene base.

GB 2224283 describes a method for obtaining artificial petrous stone for flooring and facades comprising a step of crushing marble material into particles of approximately 7 mm, a step of mixing said material with other additional materials including silica sand subjected to heating, and at least one polymerisable resin, a step of molding the mixture thus obtained with a combined action of vibration and compression under vacuum and a step of polymerizing the resin.

JP 8156216 refers to an artificial petrous product with a surface provided with a layer containing marble particles comprising a mixture of a non saturated polyester resin, calcium carbonate powder and a curing agent, obtained in molding.

JP 28111951 describes an artificial marble with a granular pattern obtained by laminating three classes of layers with resins incorporating different components such as crushed stones, ceramic, fibers, glass, etc.

Unlike the mentioned prior arts, the present invention proposes:

- a hybrid low viscosity polymer coating (in a condition prior to curing) different from those described in terms of the fact that it comprises several components of siliceous origin, particularly micronized powder and gravels of different grading bound by a polymerisable resin;

- a distribution of the components of the coating, such that a greater concentration of inorganic loads of at least 75% is obtained in the areas closest to the coating-substrate interphase, thus allowing, with a very thin layer of the order of 0.5 mm, the possibility of obtaining an efficient protection of the substrate and meeting the mechanical and chemical requirements of the substrate + coating assembly in the same or similar extent than those of a quartz or granite.

The described coating is not applied in molding, but directly on the substrate by of an applicator with retention of said coating until the complete curing thereof.

The product and method described may accomplish the goals set out below:

a) to obtain products substrate incorporating a coating with a surface having a hardness and chemical resistance comparable to quartz having similar aspect but at a lower production cost;

b) to apply a thinnest possible surface layer (thickness < 1mm);

c) enabling the use of defective or damaged slabs of marble agglomerate by applying the mentioned coating as a finish;

d) enabling to include slurries and cuttings from a marble agglomerate treatment plant or other types of waste coming from demolitions, home renovations or wastes from other industries in the composition of the base substrate or support.

Brief Description of the Invention

The hybrid polymer coating described, which can be applied to petrous or ceramic substrates, is a micro coating formed by a mixture of micronized powder and gravels of silica, quartz and/or glass of different agglomerate grading by means of a heat stable polymer and/or polymerisable thermoplastic and which enable using a substrate or base board of minimum thicknesses (4-6 mm) on which the mentioned coating that firmly adheres to the same is applied.

In greater detail, there is described a hybrid polymer coating for petrous or ceramic substrates which provides a very thin surface layer (thickness of the coating comprised between 0.1 and 2 mm and preferably less than 1 mm) firmly adhered to the substrate obtained by steps of preparing a mixture of micronized powder, one or more gravels, resin selected from polyurethane, polyester, epoxy or acrylic, catalyst and pigments, subjected to stirring, subsequent curing (with the addition or generation of heat, for example by microwaves) and final polishing of the coating consolidated on the substrate to smooth and normalize the surface.

The coating which is applied on the finished product (board or marble tile or other artificial petrous substrate) is characterized by comprising a mixture with the following composition:

- 10-25% by weight of micronized powder functioning as a cement, containing inorganic loads mainly of petrographic origin;

- 40-60% by weight of inorganic load gravels of petrous origin comprising quartz, silica, silica sand, glass, recycled mirrors, silicon, etc., of sizes comprised between 0.063 - 2 mm;

- 10-40% by weight of a base resin selected from polyurethane, polyester, epoxy or acrylic; and

- approximately 5% by weight of pigments and other additives for said resin including a catalyst.

In any case, the proportion of resin will be of at least 10-30%.

The addition of pigments of the order of 2% by weight must be understood as optional depending on the characteristics of the natural or artificial petrous substrate to which the coating would be applied.

Furthermore, the fact that it can reach a proportion of the mentioned gravel and micronized powder of the coating of up to 90% in a first inner most area (1/3 of the thickness), corresponding to the interphase between coating and surface of the petrous or ceramic substrate, of the order of 1 -15% close to the visible surface and 20-50% in a middle area, the semi-finished (i.e., non-polished) coating of this invention is distinctive considering that the same is divided into three layers of the same thickness.

In a possible embodiment, the following proportion of gravel and micronized powder could be obtained:

- lower third of the coating: between 55%-90%
- middle third of the coating: between 16%-60%;
- upper third of the coating: between 1%-15%.

According to another possible embodiment, the proportions of gravel and micronized powder would be the followings:

- lower third of the coating: between 70%-95%

- middle third of the coating: between 10%-70%;
- upper third of the coating: between 1 %-30%.

The visible surface of the coating is finished by a mechanical treatment selected from polishing with abrasives, polishing with brushes or sand blasting and/or by a chemical treatment of acid etching such that a visible surface in which first layer has been removed from the area with less gravel concentration and with more resin concentration is obtained for obtaining a final product with a very high gravel and very low resin concentration. The process of polishing further removes any particle of gravel protruding from the mixture. This step of treatment also allows working with gravels of different grading and diameters close to diameters of the thickness of the coating or final thin layer obtained (i.e., gravel sizes of 1.2 mm, for example, for a coating of 0.8 mm), since the protruding parts which could remain will be removed by polishing or equivalent mechanical treatment. Thus a hardness of the surface layer greater than 5 Mohs is obtained.

According to a preferred embodiment the mentioned mixture comprises gravels of different nature and grading.

The invention also relates to a board or petrous or ceramic substrate provided with a coating like the one mentioned and to a method for obtaining it.

In a further aspect, there is described a method for obtaining petrous or ceramic substrates having a hybrid polymer coating comprising a mixture of micronized powder, gravels, a base resin comprising one of polyurethane, polyester, epoxy and acrylic, and additives for said base resin, said coating having a thickness between 0.1 and 2 mm, characterized in that the method comprises the following steps:

a) preparing a base mixture comprising at least one first gravel of one of quartz, silica and silica sand of sizes in a range between 0.063 – 0.6mm and micronized powder with inorganic loads in a mixer;
b) stirring the base mixture;
c) preparing the base resin selected from the group consisting of polyurethane, polyester, epoxy and acrylic;
d) adding the resin to the base mixture with a catalyst, and additives for said resin, and subsequent stirring in said mixer to obtain a subsequent mixture;

e) creating a vacuum inside said mixer affecting the subsequent mixture;

f) applying a layer of a semi-fluid mixture obtained from step e) on the substrate and retaining on the substrate ;

g) vibrating the substrate to displace larger gravels towards the bottom;

h) accelerating the curing of the subsequent mixture by heating to consolidate the subsequent mixture on the substrate; and

i) finishing by a mechanical treatment comprising at least one of polishing with abrasives, polishing with brushes, sand blasting and by a chemical treatment of acid etching of the coating polymer;

wherein said subsequent mixture obtained after step d) has the following composition:

10-25% by weight of said micronized powder of siliceous materials comprising aluminium oxides, quartz and/or glass, or calcareous materials, with inorganic loads of petrographic origin;

40-60% by weight of said inorganic gravels of petrographic origin and/or comprising quartz, silica, silica sand, glass, recycled mirrors, silicon of sizes comprised between 0.063 – 0.6 mm;

10-40% by weight of a polymerizable base resin selected from polyurethane, polyester, epoxy or acrylic;

approximately 3% by weight of the additives for said resin

Other features of the invention will be seen in view of the following description of several examples of application given by way of non-limiting illustrative example according to the following detail.

Brief Description of the Drawings

Fig. 1 is a cross section micrograph detailing the four sub-areas in which the percentage of loads (particles) was visually estimated following a standard for microscopy observation.

Fig. 2 is a graph indicating the percentage of loads or load concentration (index of particles) in four differentiated areas of the coating.

Detailed Description of the Invention

The coating of the invention establishes, as a first requirement, a preferred thickness of the order of 0.5 mm (with a maximum of 2 mm) and the use of gravels of quartz or silica sand with a grain size comprised in the range of 0.1 – 0.6 mm in said preferred example, although grain sizes of 0.063 onwards has been provided.

This coating comprises, according to different tests performed the following main components:

1. Micronized powder of silica sand, quartz and/or glass functioning as a cement.

2. Gravels of quartz, glass and/or silica sand of different sizes which will confer mechanical strength to the coating

3. Polymerisable resin of polyurethane, polyester, epoxy or acrylic as a binder.

4. Additives for said resin comprising air release agents, adhesion promoters, UV absorbers, stabilizers, moistening agents to reduce viscosity (a boric acid ester solution, for example), antistatic agents, water repellents (preferably using silanes and siloxanes), self cleaning agents (using e.g., fluorocarbonated polymers), and natural and/or synthetic fibers.

5. Pigments (optional)

The selection of binder or resin used depends on the substrate to which the coating must be firmly adhered, and further determines:

- the amount of load admitted in the formulation of the coating (final viscosity of the casting) and consequently the metering equipment;
- the useful time for handling-maneuverability of the casting;
- the polymerization time and therefore the curing system;
- chemical properties, resistance to ageing, etc.

The invention proposes a hybrid polymer coating for petrous or ceramic substrates in the form of a very thin (of a thickness comprised between 0.1 and 2 mm and, preferably between 0.1 and 0.7 mm) surface layer which is arranged and is firmly adhered to the substrate, comprising a mixture of the mentioned components with the following composition:

- 10-25% by weight of micronized powder of siliceous materials comprising aluminium oxides, quartz and/or glass, or calcareous materials, with inorganic loads of petrographic origin;

- 40-60% by weight of inorganic load gravels of petrous origin and/or comprising quartz, silica, silica sand, glass, recycled mirrors, silicon, etc., of sizes comprised between 0.063 – 2 mm;

- 10-40% by weight of a polymerisable base resin selected from polyurethane, polyester, epoxy or acrylic;

- approximately 3% by weight of additives particularly catalysts for said resin;

- proportion of the mentioned gravel and micronized powder of the coating of up to 90% (and generally comprised between 55% and 85%) in one lower third or inner most area corresponding to the interphase between the coating and surface of the petrous or ceramic substrate, of the order of 1-15% in the upper third close to the visible surface and of 15- 60% in one middle third between both inner area and area adjacent to the surface.

Depending on the purpose or final location of the elements, for example, tiles obtained from the petrous board with coating, the mentioned mixture will further include up to 2% by weight of pigments.

The mentioned mixture will comprise particularly gravels of different nature and grading.

During the tests performed, the sequence and the mixture of the different ingredients of the formulation was detected as the most significant.

The order and method for preparing the mixture can be the following:

- preparing a base mixture comprising a first gravel, for example, of quartz, silica, silica sand, glass, or mirror of sizes comprised between 0.1 – 2 mm and micronized powder with inorganic loads of petrographic origin, in a mixer;
- stirring the mentioned mixture;
- preparing a base resin selected from polyurethane, polyester, epoxy or acrylic;

- adding said resin to the mentioned mixture in said mixer with a catalyst, additives and optionally pigments, and subsequent stirring;
- creating a vacuum inside said mixer;
- applying the mixture obtained on the substrate; and
- vibrating the substrate with the mixture applied on top of the same on a vibration table.
- controlled supplying of thermal energy for curing of the mixture, retained on the substrate.

Referring to the preparation of the resins, if it is an acrylic resin: an acrylic resin diluted in methyl methacrylate + coupling agent of siliceous origin + air release agent + humectant (if necessary) + catalyst) can be used.

If it is a polyurethane resin: a mixture of polyisocyanates + polyol + coupling agent of siliceous origin + water capturing molecular sieve + catalyst) can be used.

And, if it is an epoxy-type resin: a resin with epoxy groups + coupling agent of siliceous origin + air release agent + accelerant (if necessary) + epoxy resin cross linking agent (amines, anhydrides, carboxylic acids, etc.) can be used.

In the laboratory tests, the components have been mixed by means of a rod stirrer and in the pilot plant tests with a screw mixer.

In the field, the mixture may be prepared by continuous mixing in a screw extruding machine in which all the gravels and powder are loaded, and liquid material comprising the resin, the catalyst, and other additives are injected in a subsequent section of the path of the screw.

In an exemplary embodiment, the mixture obtained from the mixture has a Brookfield viscosity at room temperature in the range of 4,350 to 4,440 mPas corresponding to a shearing speed of 30-20 rpm.

The coating applied on the indicated artificial petrous substrate has its surface finished by a mechanical treatment which can be polishing with abrasives, polishing with brushes or sand blasting and substituted or completed by a chemical treatment of acid etching.

After the curing, a step of cutting the substrate with the consolidated coating into plates with a specific format or eventually in the form of tiles has also been provided.

Tests: Samples of substrate with coating produced according to the method

Two samples formed by respective square-shaped agglomerated stone specimens of dimensions 15 x 15 x 1.4 cm^3 with an applied surface hybrid polymer coating like the one described were used. The samples therefore comprise a substrate with the described consolidated coating (i.e., it is a sample with the vibrated, cured and polished mixture).

The visual study of the inorganic particle dispersion was carried out by Scanning Electron Microscopy (SEM). To perform quantitative and representative estimation of the sample, the specimen was transversely cut and micrographs were made in 6 different areas, reflecting in each case the coating/substrate interphase.

Then, in each micrograph four sub-areas in which the percentage of particles was visually estimated following a standard for microscopy observation (Figure 1) were differentiated.

Generally, an increase in the accumulation of the inorganic particles is observed in the areas closest to the interphase, having in turn the largest particle sizes (estimated between 70 and 80%), although the dispersion of loads is rather homogenous. Contrarily, the area closest to the surface has lower particle index and smaller particles, estimating a load distribution between 5 and 15% (Figure 2).

If the average results calculated from the percentage of loads for each studied area are analyzed, the existence of a tendency for the accumulation of loads towards the inner most areas of the coating (Table 1 and Figure 2) is confirmed.

TABLE 1

Table 1: Estimation of the amount of gravel in differentiated areas

Area	AVERAGE GRAVEL AMOUNT (%)	
	Vibrated sample	Non-vibrated sample
Upper (1)	9	13
Upper-center (2)	23	18
Lower-center (3)	37	36
Lower (4)	78	62

As has been indicated above, the mixture in the form of a semi-fluid mass is distributed on the board taking advantage of its relative fluidity. In the example discussed, the board has been provided with advantageously anti-adherent side partitions retaining the mixture during the step of vibrating thereof on the board.

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

1.- A method for obtaining petrous or ceramic substrates having a hybrid polymer coating comprising a mixture of micronized powder, gravels, a base resin comprising one of polyurethane, polyester, epoxy and acrylic, and additives for said base resin, said coating having a thickness between 0.1 and 2 mm, characterized in that the method comprises the following steps:

a) preparing a base mixture comprising at least one first gravel of one of quartz, silica and silica sand of sizes in a range between 0.063 – 0.6mm and micronized powder with inorganic loads in a mixer;

b) stirring the base mixture;

c) preparing the base resin selected from the group consisting of polyurethane, polyester, epoxy and acrylic;

d) adding the resin to the base mixture with a catalyst, and additives for said resin, and subsequent stirring in said mixer to obtain a subsequent mixture;

e) creating a vacuum inside said mixer affecting the subsequent mixture;

f) applying a layer of a semi-fluid mixture obtained from step e) on the substrate and retaining on the substrate ;

g) vibrating the substrate to displace larger gravels towards the bottom;

h) accelerating the curing of the subsequent mixture by heating to consolidate the subsequent mixture on the substrate; and

i) finishing by a mechanical treatment comprising at least one of polishing with abrasives, polishing with brushes, sand blasting and by a chemical treatment of acid etching of the coating polymer;

wherein said subsequent mixture obtained after step d) has the following composition:

10-25% by weight of said micronized powder of siliceous materials comprising aluminium oxides, quartz and/or glass, or calcareous materials, with inorganic loads of petrographic origin;

40-60% by weight of said inorganic gravels of petrographic origin and/or comprising quartz, silica, silica sand, glass, recycled mirrors, silicon of sizes comprised between 0.063 – 0.6 mm;

10-40% by weight of a polymerizable base resin selected from polyurethane, polyester, epoxy or acrylic;

approximately 3% by weight of the additives for said resin.

2. The method according to claim 1, wherein the proportion of said gravel and micronized powder with respect to the thickness of the coating along three layers of said coating having the same thickness is the following:

- in a lower third of the coating, corresponding to the first inner most area at the interface between the coating and the surface of the petrous or ceramic substrate, said gravel and micronized powder are in a range between 55%-85% by weight;

- in a middle third of the coating said gravel and micronized powder are in a range between 15%-60% by weight; and

- in an upper third of the coating, close to the visible surface of the coating, said gravel and micronized powder are in a range between 1%-15% by weight.

3. The method according to claim 1, characterized in that the gravels comprise gravels selected by their sizes comprised between 0.1 and 0.5 mm.

4. The method according to claim 1, characterized in that in said first step for forming the mixture, a plurality of gravels of different sizes and of the same or different materials are used.

5. The method according to any one of claims 1 to 4, characterized in that step d) includes adding at least one pigment.

6. The method according to claim 5, characterized in that the subsequent mixture after step d) includes up to 2% by weight of pigments.

7. The method according to claim 1, characterized in that said mixture is prepared according to a process of continuously mixing in a screw extruding machine in which all the gravels and powder are loaded, injecting liquid materials comprising the resin, the catalyst, and the additives in a subsequent section of the path of the screw.

8. The method according to claim 1, characterized in that the step f) of applying the mixture on the substrate is performed with an applicator retaining a layer of mixture on said substrate and which is maintained during the step of curing.

9. The method according to claim 1, characterized in that the Brookfield viscosity at room temperature of the mentioned mixture obtained from the mixer is comprised between 4,350 and 4,440 mPas corresponding to a shearing speed of 30-20 rpm.

10. The coating obtained by the method of any one of claims 1 to 9, characterized in having a hardness greater than 5 Mohs.

11. A petrous or ceramic substrate incorporating on a visible surface, a coating obtained by the method of any one of claims 1 to 9

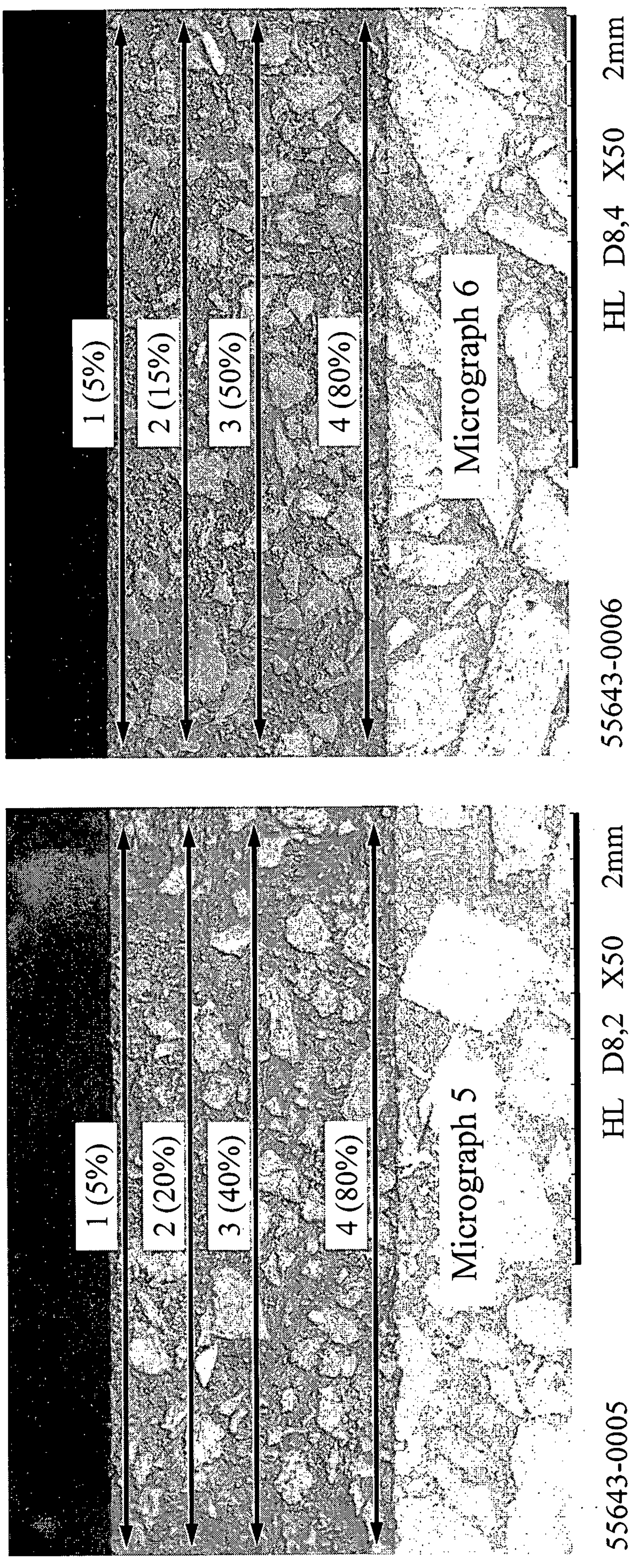
1 (5%)
2 (15%)
3 (50%)
4 (80%)
Micrograph 6
55643-0006
HL D8,4 X50 2mm
1 (5%)
2 (20%)
3 (40%)
4 (80%)
Micrograph 5
55643-0005
HL D8,2 X50 2mm

Fig. 1

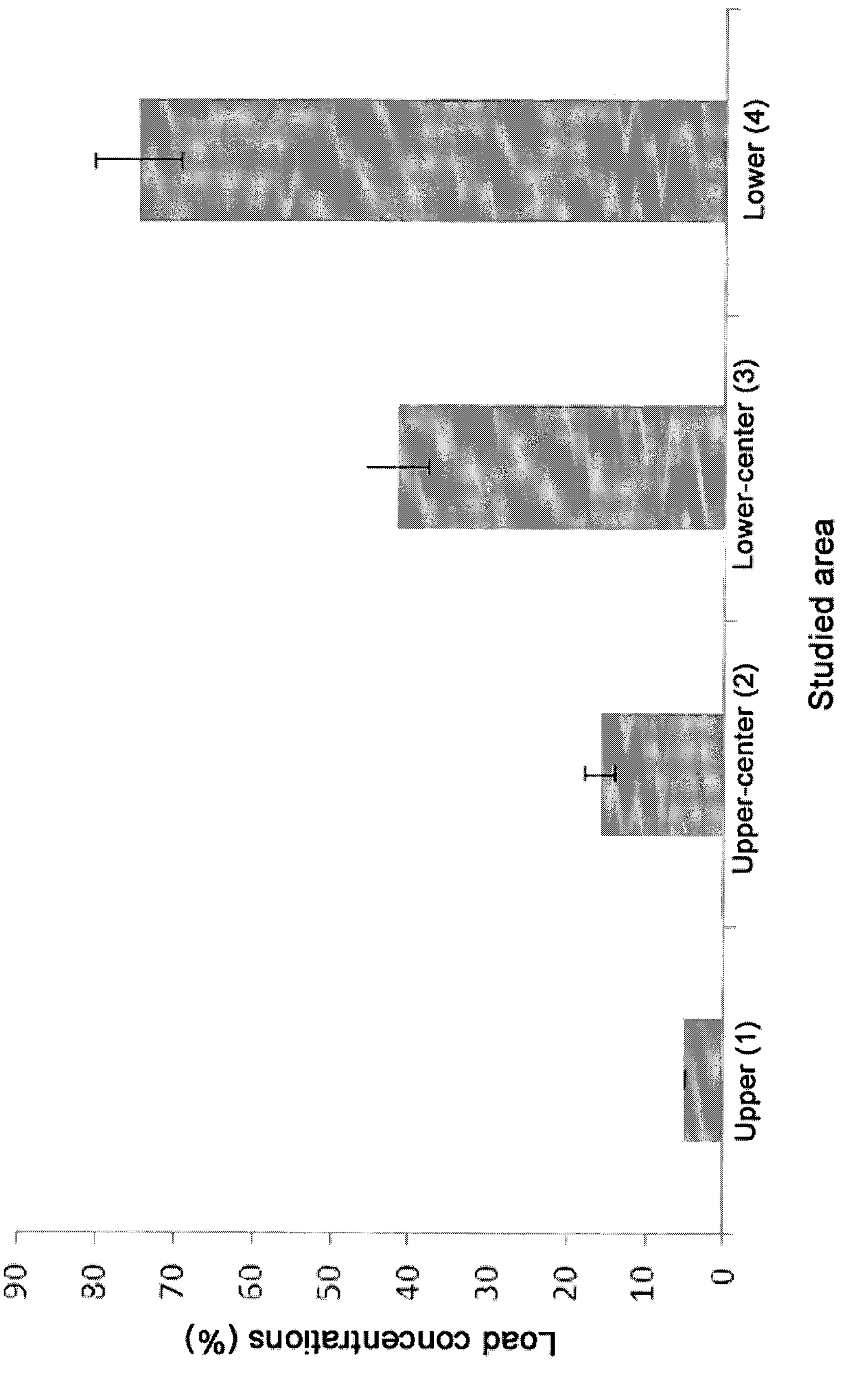
Load concentrations (%)
0
10
20
30
40
50
60
70
80
90
Upper (1)
Upper-center (2)
Lower-center (3)
Lower (4)
Studied area

Fig. 2