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(54) **Title**: COMPOSITIONS FOR THE SANITIZING ANTI-POLLUTION, WATER AND OIL REPELLENT, PROTECTIVE AND POLISHING TREATMENT OF STONE MATERIALS, THEIR PREPARATION AND USE

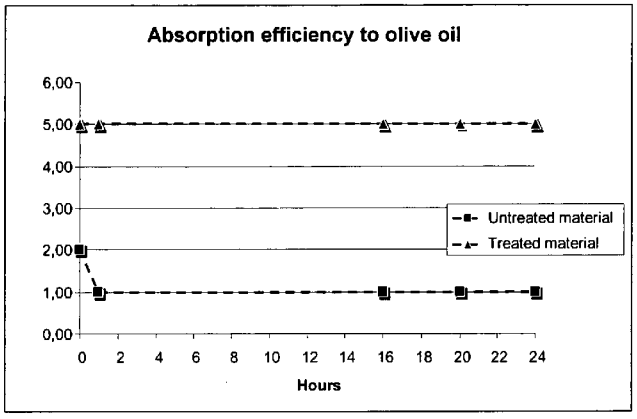

FIG. 1

(57) **Abstract**: There are described compositions based on polyester, epoxy, polyurethane, fluoropolymer resins and silicone resins in general in all forms and also in photosensitive form utilizable to improve the appearance and hygiene properties of stone surfaces, processes for their preparation and use.

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COMPOSITIONS FOR THE SANITIZING, ANTI-POLLUTION, WATER AND OIL REPELLENT, PROTECTIVE AND POLISHING TREATMENT OF STONE MATERIALS, THEIR PREPARATION AND USE.

Field of the invention

The present invention relates to the field of products for the treatment of stone surfaces.

State of the art

Processing of stone and concrete derivatives, in general in the form of slabs and marble chips, in the majority of cases requires the surfaces to be treated with resin or the application of coatings and/or impregnating agents in order to protect the materials from dust, liquids, moulds and stains in general, and to repair imperfections such as fractures, porosity, splitting, cavities, etc.

Moreover, there is increasing demand for the surfaces of these materials to have antibacterial properties, also in view of the decrease in hygiene standards due to the increase in the volumes of goods handled and to the variety of their sources.

Besides these needs, which are intrinsic to the use of the aforesaid materials, a quality required of the surfaces of these materials is that they contribute towards decreasing atmospheric pollution.

Currently, after resin coating or final treatment of the materials additional treatments are required to obtain the aforesaid qualities, in which the surfaces are treated with products capable of performing the aforesaid action (such as solutions containing TiO_2, the photocatalytic and antibacterial properties of which are well-known).

In view of the above, there is obviously an interest in developing products that allow the desired effects to be obtained without the additional treatments currently necessary and at the same time without having to substantially modify the technological process currently employed in operations to perform resin coating or final treatment of materials with any surface finish.

Brief description of the Figures

Figure 1 is a graph showing the absorption efficiency to olive oil of a surface treated with a composition according to the invention.

Figure 2 is a graph showing the absorption efficiency to Coca Cola® of a surface

treated with a composition according to the invention.

Figure 3 is a graph showing the absorption efficiency to coffee of a surface treated with a composition according to the invention.

Summary of the invention

The present invention relates to the production of polyester, epoxy, polyurethane, fluoropolymer resins and silicone resins in general, also in photosensitive form or their mixtures, with antimicrobial, anti-mould and photocatalytic properties combined with water-oil repellent, protective and polishing properties.

Detailed description of the invention

The present invention allows the aforesaid problems to be overcome through the use of polyester, epoxy, polyurethane, fluoropolymer resins and silicone resins in general, also in photosensitive form or mixtures thereof, containing TiO_2, or CuO and/or Ag.

Stone materials according to the invention are intended as: marbles, granites, natural stones and their aggregate derivatives, while concrete derivatives are intended as all those products in solid state in which the binder is mixed with water and if necessary with aggregates with various grain sizes.

Polyester resins are intended as those commercially available generally obtained through esterification of a mixture of a saturated dibasic acid and of an aliphatic acid with aliphatic glycols; the epoxy resins utilized according to the invention are also those commercially available of the photosetting or thermosetting type obtained through condensation of bisphenol and epichlorhydrine.

Fluoropolymers are intended as those commercially available resins (both water and solvent based) containing compounds based on fluorite in its various forms (PTFE, PVDF, PFA, FEP etc.), and in particular acrylic and non-acrylic fluorinated copolymers. Some of these resins are commercially and generically called Teflon®.

Silicone resins are intended as those commercially available resins (both water and solvent based) composed in general by cage-like oligosiloxanes (commercially called silanes or siloxanes in general) in the general formula of the type $R_nSiX_mO_y$, where R is a non-reactive group (typically Methyl or Phenyl group) and X is a functional group (H, OH, Cl or alkoxyl group) and where n = 0, 1, 2, 3, 4;

m = 0, 1, 2, 3, 4; Y = 0, 1, 2, 3, 4

TiO_2 according to the invention is intended both as the oxide in powder form and dispersions or suspensions thereof, such as colloidal dispersions, in water or other solvents, such as 2-propanol, 1,2-Propanediol, Ethylene Glycol etc.; the oxide can either be in Anatase or Rutile form.

Ag can also be utilized both as a metal powder and in dispersions or suspensions, such as colloidal dispersions, in water or other solvents, such as 2-propanol, 1,2-Propanediol, Ethylene Glycol etc.; if preferred inert carriers such as Zeolite can be used; in particular in formulations containing Fluoropolymers or silicone resins, the Ag is present in ionic or metallic form.

CuO according to the invention is intended both as the oxide in powder form and in dispersions or suspensions, such as colloidal dispersions, in water or other solvents, such as 2-propanol, 1,2-Propanediol, Ethylene Glycol etc..

The compounds according to the invention normally contain a quantity in weight of TiO_2 or CuO between 0.03% and 10%, preferably 0.2% with respect to the resin.

The quantity in weight of Ag is between 0.0002% and 2%, preferably 0.05% with respect to the resin in the case of pure Ag.

Employing inert carriers such as Zeolite for the Ag, their quantity in weight is between 0.1% and 15%, preferably 2.5% with respect to the resin.

In the case of dispersions of Ag in ionic form the quantity is between 0.0002 % and 5%

To prepare the compositions according to the invention, the dispersions or powders defined above, obtained on the market or prepared according to known methods, are added to the resins as defined above, also obtained on the market or prepared according to essentially known techniques as described above.

The resins thus obtained are applied either prior to, or in an intermediate step of, the smoothing or polishing process, to eliminate defects and control the porosity of the stone materials; they allow the appearance and properties of finished or semi-finished stone and cement products to be improved, also making the surfaces sanitizing, easy to maintain and purifying for the surrounding environment.

The resins according to the invention can also be used directly in the production processes of aggregates, which employ them as binder.

The examples below show how the resins according to the invention were obtained.

Example 1

Photocatalytic epoxy resin

The following quantities of raw materials were added to a plastic beaker positioned on a magnetic stirrer under constant stirring using a magnetic bar:

99 g Bond epoxy resin Industrial Chem Italia

1 g Dispersion in 1.2 propandiol of nanometric Rutile TiO2 15 nm 20% in weight

The following was added after approximately one hour under constant stirring

46 g Hardener Bond Industrial Chem Italia

Subsequently, the product was applied to marble chip using a brush and left to dry for approximately 48 hours.

Example 2

Antibacterial epoxy resin

The following quantities of raw materials were added to a plastic beaker positioned on a magnetic stirrer under constant stirring using a magnetic bar:

96 g Bond epoxy resin Industrial Chem Italia

4 g Ag in zeolite powder

The following was added after approximately one hour under constant stirring

46 g Hardener Bond Industrial Chem Italia

Subsequently, the product was applied to marble chip using a brush and left to dry for approximately 48 hours.

Example 3

High penetration antibacterial epoxy resin

The following quantities of raw materials were added to a plastic beaker positioned on a magnetic stirrer under constant stirring using a magnetic bar:

76 g Bond epoxy resin Industrial Chem Italia

25 g Fluid Bond fluidifier Industrial Chem Italia

4 g Ag in Zeolite powder

The following was added after approximately one hour under constant stirring

46 g Hardener Bond Industrial Chem Italia

Example 4

Water-based antibacterial water and oil repellent product

The following quantities of raw materials were added to a plastic beaker positioned on a magnetic stirrer under constant stirring using a magnetic bar:

80 g of distilled water

20 g fluoropolymer Sil 87

0.2 g nanometric Ag aqueous suspension 5%

0.1 g Ag ion solution 2.5%

The resins thus obtained were applied to a stone aggregate in the intermediate polishing step (examples 1-2 and 3) and to polished granite (example 4).

The antibacterial tests (48 h in oven with Plate Count Agar (PCA) culture media for psychrophilic bacteria count and Sabouraud Agar + Chloramphenicol (SAB c) total fungal count with inhibition of contaminating bacterial flora), were performed on samples taken to final polishing normally exposed to natural radiation on a day that was not particularly sunny with the following results:

Resin according to example 1

PCA: 1 CFU/plate = 0.02 CFU/cm2

SAB: 0 CFU/plate = 0 CFU/cm2

Resin according to example 2

PCA : 19 CFU /plate = 0.45 CFU/cm2

SAB: 7 CFU/plate = 0.2 CFU/cm2

Resin according to example 3

PCA : 35 CFU/plate = 0.6/cm2

SAB: 14 CFU/plate = 0.4/cm2

Resin according to example 4 (applied to sample of "Kashmir White" polished granite)

PCA : 42 CFU/plate = 0.7/cm2

SAB: 22 CFU/plate = 0.4/cm2

The resin according to example 4 was also tested for oil repellency and resistance to Coca Cola® and coffee according to the standard ASTM D1308 with results shown in the accompanying graphs.

Comparing the CFU values measured with the IMA table of limit values indicated

in the INAIL (national institute for insurance against industrial accidents) guidelines for microbiological monitoring of workplaces, it can be seen that:

a) performances of the resin according to example 1 in the presence of adequate irradiation are compatible with use in ultra clean rooms (protective isolation, operating theatres for ear prostheses, some electronic and pharmaceutical industry processes);

b) performances of the resin according to example 2 are compatible with use in clean rooms (operating theatres for general surgery, intensive care, dialysis, some electronic and pharmaceutical industry processes, microbiology laboratories);

c) performances of the resin according to example 3 are compatible with use in doctor's surgeries, laboratories, food industries, kitchens, restaurants, factories;

d) performances of the resin according to example 4 are compatible with use in doctor's surgeries, laboratories, food industries, kitchens, restaurants, factories.

The resin also shows exceptional resistance to absorption of oil and Coca Cola® and high resistance to absorption of coffee.

CLAIMS

1. Compositions for the treatment of stone surfaces or materials comprising polyester, epoxy, polyurethane, fluoropolymer resins and silicone resins in general, also in photosensitive form or their mixtures, containing TiO_2, or CuO and/or Ag.
2. Compositions according to claim 1, wherein said polyester resins are conventional resins obtained through esterification of a mixture of a saturated dibasic acid and of an aliphatic acid with aliphatic glycols.
3. Compositions according to claim 1, wherein said polyester resins utilized are conventional resins of the photosetting or thermosetting type obtained through condensation of bisphenol and epichlorhydrine.
4. Compositions according to claims 1 - 3, wherein said TiO2 or CuO is composed of oxide in powder form or dispersions or suspensions thereof in water or other solvents.
5. Compositions according to claims 1 - 4, wherein the Ag is composed of a metallic powder or dispersions or suspensions thereof in water or other solvents, if necessary in the presence of inert carriers or is present in ionic form.
6. Composition according to claim 1 - 5, wherein the quantity in weight of TiO_2 or CuO is between 0.03% and 10%, preferably 0.2% with respect to the resin.
7. Composition according to claims 1 - 6, wherein the quantity in weight of Ag is between 0.0002% and 2%, preferably 0.05% with respect to the resin in the case of pure Ag, while when carriers are used their quantity in weight is between 0.1 – 15%, preferably 2.5% with respect to the resin.
8. Composition according to claims 1 - 6, wherein the Ag is present in ionic form and in quantities between 0.0002 % and 5%.
9. Process for the preparation of resins according to claims 1 – 8, wherein said dispersions or said powders are added to said resins according to known methodologies.
10. Process for the treatment of stone materials wherein the compositions according to claim 1 – 8 are applied prior to, or in an or in an intermediate step of, the smoothing or polishing process, of the stone material.

11. Process according to claim 10, wherein said stone materials are marbles, granites, natural stones, their aggregate derivatives, and concrete derivatives.
12. Concrete derivatives comprising the compositions according to claims 1 – 8 as binders.
13. Process for the production of concrete derivatives according to claim 12 wherein the resins according to claims 1 – 8 are employed directly as binders to form the relative aggregates.

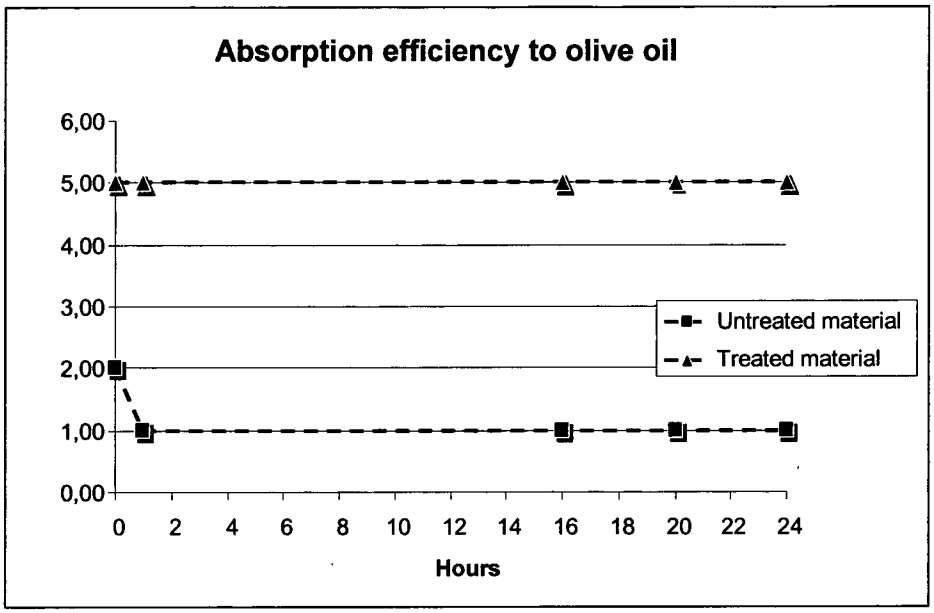
Absorption efficiency to olive oil
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0 2 4 6 8 10 12 14 16 18 20 22 24
Hours
Untreated material
Treated material

FIG. 1

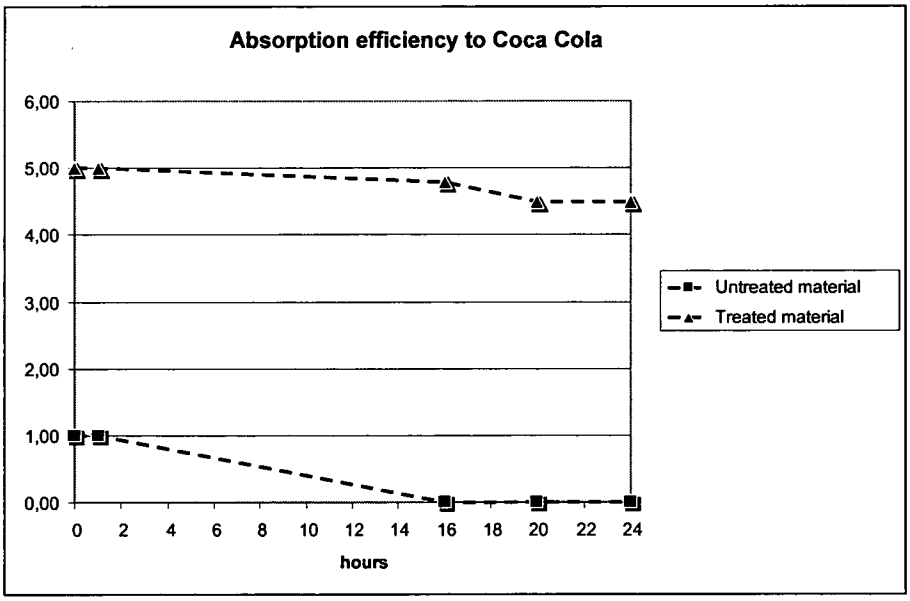
Absorption efficiency to Coca Cola
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0 2 4 6 8 10 12 14 16 18 20 22 24
hours
Untreated material
Treated material

FIG. 2

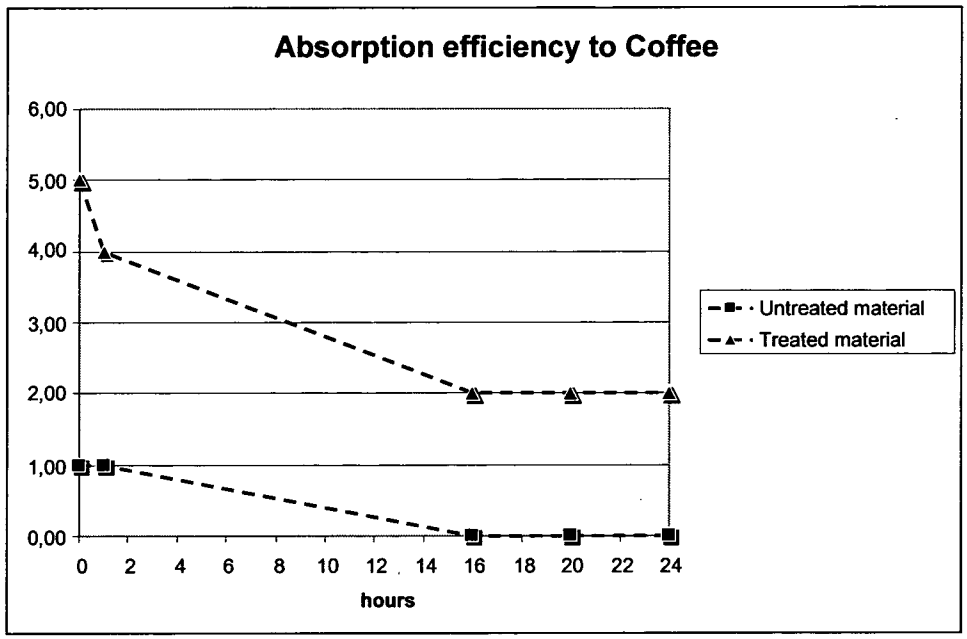
Absorption efficiency to Coffee
6,00
5,00
4,00
3,00
2,00
1,00
0,00
0 2 4 6 8 10 12 14 16 18 20 22 24
hours
Untreated material
Treated material

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2008/053933

A. CLASSIFICATION OF SUBJECT MATTER
INV. C04B41/48 C04B26/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 2007/077406 A1 (JACOBS JEFFRY L [US] ET AL) 5 April 2007 (2007-04-05) examples	1-13
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
6 May 2009	19/05/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Rosenberger, Jürgen

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International application No
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