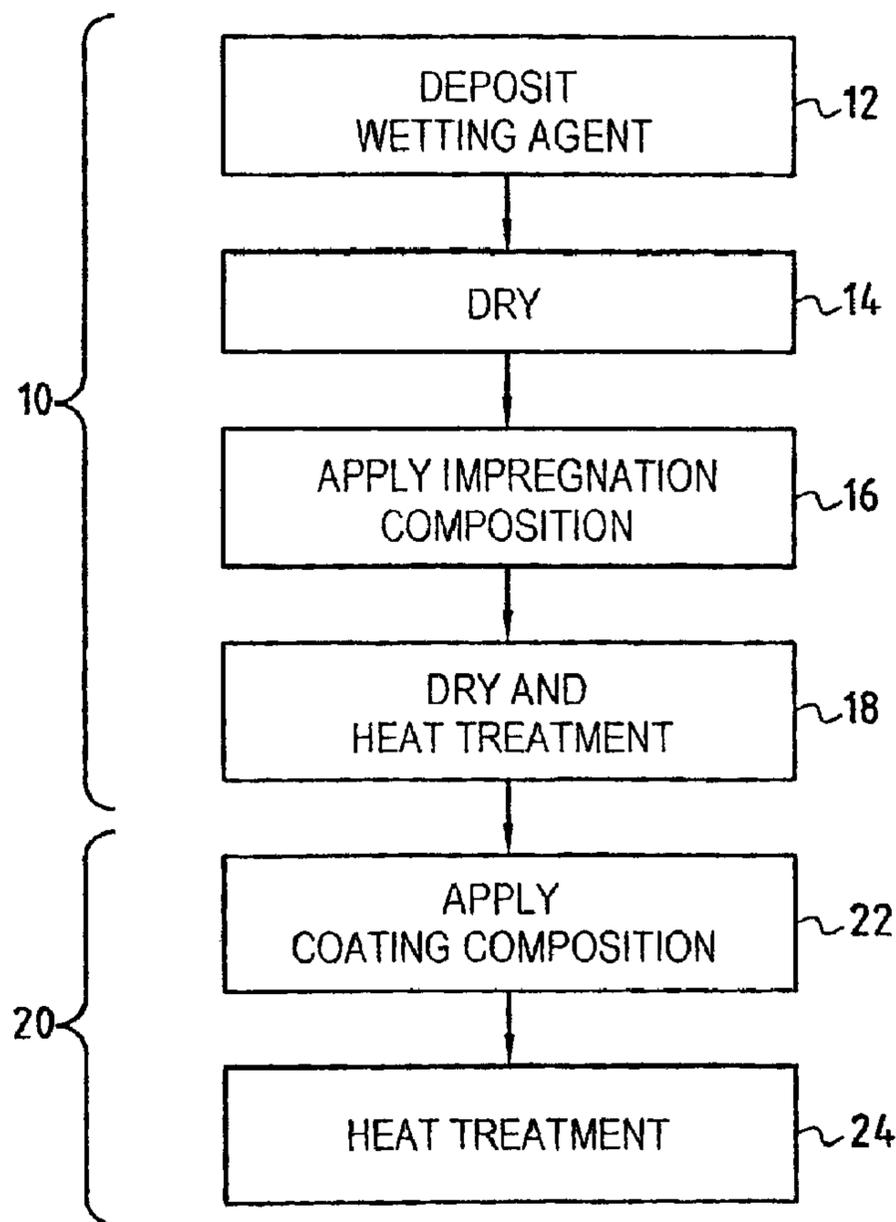




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 (72) Inventeurs/Inventors:
 NICOLAUS, NATHALIE, FR;
 FONTARNOU, VERONIQUE, FR;
 ROUSSARIE, NADIA, FR
 (73) Propriétaire/Owner:
 MESSIER-BUGATTI-DOWTY, FR
 (74) Agent: SIM & MCBURNEY

(54) Titre : PROTECTION ANTI-OXYDATION DE PIECES EN UN MATERIAU COMPOSITE CONTENANT DU CARBONE
 (54) Title: ANTI-OXIDATION PROTECTION OF PIECES MADE FROM A COMPOSITE MATERIAL CONTAINING
 CARBON



(57) Abrégé/Abstract:

The method comprises the steps of: - impregnating the part with a liquid impregnation composition containing at least a phosphate type compound, via at least a fraction of the outside surface of the part; - applying a coating composition on said fraction of the



(57) **Abrégé(suite)/Abstract(continued):**

outside surface of the part, the coating composition comprising a colloidal solution of at least one refractory oxide in water, at least one compound essentially of the borosilicate type in powder form and having healing properties, and at least one metallic boride in powder form; and - applying heat treatment after applying the coating composition.

A B S T R A C T

The method comprises the steps of:

- 5 - impregnating the part with a liquid impregnation composition containing at least a phosphate type compound, via at least a fraction of the outside surface of the part;
- 10 - applying a coating composition on said fraction of the outside surface of the part, the coating composition comprising a colloidal solution of at least one refractory oxide in water, at least one compound essentially of the borosilicate type in powder form and having healing properties, and at least one metallic boride in powder form; and
- 15 - applying heat treatment after applying the coating composition.

Title of the invention

Anti-oxidation protection of pieces made from a composite material containing carbon.

5 Background of the invention

The invention relates to providing protection against oxidation for parts made of a carbon-containing composite material, i.e. parts made of a material comprising fiber reinforcement densified by a matrix and
10 in which carbon is present at least in the fiber reinforcement, or in the matrix, or indeed in an interphase between the reinforcing fibers and the matrix. A particular field of application for the invention lies in protecting parts made of carbon/carbon (C/C) composite
15 material against oxidation, and in particular brake disks for aircraft.

In an oxidizing medium, the capacity of such parts to retain good mechanical properties at high temperatures depends on providing effective protection against the
20 carbon being oxidized. After it has been made, the composite material inevitably presents residual internal pores, which pores provide the surrounding medium with access to the core of the material.

A well-known process for protecting carbon parts
25 against oxidation consists in forming an outer coating of ceramic, in particular of silicon carbide SiC. Nevertheless, such coatings are often fragile and liable to cracking, and they cannot perform the function of providing a protective barrier against the oxygen of the
30 surrounding medium in the long term.

US Patent No. 6,455,107 proposes to form an external coating by using a dispersing means such as colloidal silica containing refractory powders, mainly SiC powder, and other powders such as titanium diboride TiB₂, silicon
35 nitride Si₃N₄ and molybdenum disilicide MoSi₂. The object is to form a thick external protective coating, having typically a thickness of 500µm, and adhering to carbon,

in particular for elements of electrochemical cells, with elements enhancing electrical conductivity, in particular metallic particles, being advantageously added.

5 US patent No. 4 931 413 proposes forming an outer coating from a composition that is a precursor for a glass ceramic that is capable of constituting a leakproof coating. That composition is made of a mixture of titanium diboride powder TiB_2 and of colloidal silica, possibly together with additional SiC powder.

10 In certain applications, the protection against oxidation provided to parts made of carbon-containing composite material must also retain its effectiveness even in the presence of moisture and/or of carbon oxidation catalysts. This applies in particular for
15 airplane brake disks which can be exposed to the moisture present in runways, and which can come into contact with oxidation catalysts present in the de-icing compositions used on airport runways.

To provide better protection against catalytic
20 oxidation of carbon, it is known to use internal protection based on one or more metal phosphates put into place by impregnating composite material parts with a composition in the form of an aqueous solution. In-depth impregnation within the pores of the material can be made
25 easier by the presence of a wetting agent (or surfactant) mixed in the impregnation composition, or applied beforehand. Reference can be made in particular to US patent No. 5 853 821.

Such internal protection is effective up to a
30 threshold temperature above which its active elements decompose. In order to extend the range of protection to higher temperatures, proposals have been made also to form an outer coating on the surfaces of the parts.

The outer coating can then be in the form of a
35 ceramic layer, e.g. of SiC. Thus, patent document WO 97/42135 describes a method of providing C/C composite material parts with protection against oxidation, in

which internal protection containing aluminum and zinc phosphates is combined with external protection of SiC obtained by applying colloidal silica, drying, and performing heat treatment at high temperature (1600°C to 1800°C) so as to form SiC by chemical reaction between the silica and the carbon of the composite material. Nevertheless, as mentioned above, an SiC coating has difficulty in providing long-lasting sealing against the surrounding medium.

US patent No. 6 740 408 proposes forming an outer coating having self-healing properties, i.e. having the ability of passing to a viscous state at the utilization temperatures of the parts, thereby plugging any possible cracks so as to form an effective barrier against diffusion of oxygen from the surrounding medium. The coating is obtained from a coating composition comprising a mixture of a powder of a borosilicate type vitreous compound, TiB_2 powder, and a binder comprising a ceramic precursor resin in solution in a solvent, typically a polycarbosilane (PCS) resin in solution in xylene. After the coating composition has been applied, steps of drying (elimination of solvent) and of curing the resin are performed. The polymer that is obtained by curing the resin is transformed into a ceramic by heat treatment, either before the parts are used, or on first exposure of the parts to high treatment on being used.

That method provides a real improvement in protection against oxidation at high temperatures because of the self-healing properties of the outer coating, due to the presence of the borosilicate type vitreous compound, i.e. essentially comprising the oxides B_2O_3 and SiO_2 . The TiB_2 constitutes an oxide reservoir for regenerating the B_2O_3 which tends to become volatile when the temperature reaches 400°C to 500°C. The oxide TiO_2 is also generated likewise compensating for the loss of B_2O_3 and increasing the viscosity of the vitreous compound, while preserving its self-healing ability.

Nevertheless, the use of a PCS resin in solution in xylene presents drawbacks. Xylene is inflammable and toxic and evaporates very fast on drying, thereby posing environmental and safety problems. In addition, the PCS
5 needs to be cured in a controlled manner that is difficult to perform insofar as it determines the quality of the final protection.

Object and summary of the invention

10 An object of the invention is to remedy the above-mentioned drawbacks, and for this purpose the invention provides a method of providing protection against oxidation for a part made of composite material containing carbon and presenting open internal pores in
15 particular for a C/C composite brake disk for aircraft, the method including the steps of:

- 20 - impregnating the part with a liquid impregnation composition containing at least a phosphate type compound, via at least a fraction of the outside surface of the part;
- applying heat-treatment to the impregnated part to form internal protection against oxidation of the type comprising phosphate anchored within the composite material;
- 25 - applying a coating composition on said fraction of the outside surface of the part, the coating composition comprising a colloidal solution of at least one refractory oxide in water, at least one compound essentially of the borosilicate type in powder form and
30 having healing properties, and at least one metallic boride in powder form; and
- applying heat treatment after applying the coating composition.

The method of the invention has several significant
35 advantages.

Thus, the carrying out of method does not require solvent that is difficult to handle, nor does it require a resin to be cured and is then particularly easy.

In addition, as shown below, the resulting coating in association with the internal protection, confers exceptional resistance to oxidation on the composite material.

The presence of a vitreous compound having self-healing properties in the mixture of colloidal solution of refractory oxide with metallic boride leads to mixed glasses to be formed during the thermal cycles which the composite material is exposed to during use, which confers to the coating an effective role of protective barrier towards the oxygen of the surrounding medium, as well as a high hardness contributing to the integrity of the coating.

In addition to a function of dispersing mineral loads that are added thereto, the colloidal solution contributes to the sealing of the porosity of the composite material, due to the nanometric particles of refractory oxide being present, and contributes to the formation of glass due to the refractory oxide being present.

Advantageously, a colloidal solution is used which is basic such as a colloidal solution stabilized by means of an added basic compound, which allows a strong bonding to the internal protection of phosphate type which has an acid character. A good bonding of the external protective coating to the composite material part is thus achieved, which is important for a part exposed to high mechanical forces as in the case of a brake disk for an aircraft. In addition to the above mentioned functions, the colloidal solution contributes then to the adherence of the protective coating.

The coating composition preferably comprises, by weight:

25% to 50% of aqueous colloidal solution of refractory oxide with a concentration in refractory oxide lying preferably in the range 25% - 50%;

5% to 20% of a powder of a vitreous compound essentially
5 of the borosilicate type;

30% to 60% of a metallic boride powder, and the possible remainder being water.

Advantageously, a coating is formed which, after heat treatment, has a relatively small thickness, preferably in the
10 range 50 μ m to 250 μ m, more preferably in the range 50 μ m to 150 μ m.

Preferably, a first heat treatment is performed after impregnation with the impregnation composition, and a second heat treatment is performed after application of the coating
15 composition. Advantageously, the second heat treatment is performed under an oxidizing atmosphere at high temperature for a relatively short duration.

The or each phosphate type compound of the impregnation composition may be selected in particular from the phosphates
20 of aluminum, zinc, manganese, magnesium, and calcium. For example it is possible to use aluminum metaphosphate.

The colloidal solution may comprise at least one oxide selected from the oxides of silicon, titanium, vanadium, yttrium, and zirconium, in particular silica SiO₂.

25 One or more metallic borides in powder form selected from the borides of titanium, vanadium, zirconium, and hafnium may be used, in particular TiB₂.

In accordance with an aspect of the present invention, there is provided a method of providing protection against
30 oxidation for a part made of composite material containing carbon and presenting open internal pores, the method comprising the steps of:

- impregnating the part with a liquid impregnation composition containing at least a phosphate compound, via at least a fraction of the outside surface

of the part;

5 - applying a coating composition on said fraction of the outside surface of the part, the coating composition comprising a refractory oxide in an aqueous solution of colloidal silica, at least one compound essentially of a borosilicate in powder form and having healing properties, and
10 at least one boride selected from the borides of titanium, vanadium, zirconium, and hafnium in powder form; and

- applying heat treatment after applying the coating composition, wherein the coating composition comprises:

15 25 wt% to 50 wt% of the aqueous solution of colloidal silica with a concentration of refractory oxide lying in the range 25 wt% to 50 wt%;

5 wt% to 20 wt% of the at least one compound essentially of a borosilicate in powder form;

20 30 wt% to 60 wt% of the at least one boride in powder form, and 0 to 20 wt% of water.

Brief description of the drawing

Other features and advantages of the method of the invention appear on reading the following description provided
25 by way of non-limiting indication and made with reference to the accompanying drawing, in which:

- Figure 1 shows the successive steps in an implementation of a method of the invention; and

- Figure 2 is a fragmentary face view of a brake disk of C/C composite material.

Detailed description of embodiments

5 The description below relates to protecting C/C composite material parts against oxidation, and more particularly to protecting brake disks for aircrafts.

10 In the embodiment of the method represented by Figure 1, a first stage 10 consists in impregnating a part or a portion of a part made of C/C composite material that is to be protected against oxidation with an impregnation composition that is suitable for forming internal protection and comprising at least one metallic phosphate, in particular for the purpose of providing
15 protection against catalytic oxidation of the carbon.

 Advantageously, the procedure is as described in US patent No. 5 853 821. A first step 12 consists in depositing a wetting agent within the accessible pores of the composite material. For this purpose, an aqueous
20 solution of a wetting agent is used, e.g. the product sold by the German supplier Hüls under the name "Marlophen NP9". After impregnation with the aqueous solution of the wetting agent followed by drying (step 14), an impregnation composition in the form of an
25 aqueous solution containing at least one metallic phosphate is applied to the outside surface of the part, or selectively to determined zones of said surface using a brush or a spray (step 16). For example, the solution used is an aqueous solution of aluminum
30 dihydrogenphosphate $\text{Al}(\text{H}_2\text{PO}_4)_3$. The wetting agent present on the surfaces of the pores facilitates penetration of the impregnation composition. Drying followed by heat treatment up to about 700°C in a non-oxidizing atmosphere are then performed (step 18), leading to the surfaces of
35 the accessible pores being coated in a C/C composite material to provide internal protection against oxidation.

For a brake disk 30 made of C/C composite material, as shown in Figure 2, the application of the impregnation composition can be restricted to the non-rubbing outer surfaces (shaded zone in the figure), while the annular friction surface or both annular friction surfaces on opposite sides of the disk are not impregnated in order to avoid spoiling their tribological properties.

A second stage 20 consists in forming an outer coating having self-healing properties.

For this purpose, a coating composition is used that comprises: at least one refractory oxide in colloidal solution in water; a borosilicate type vitreous compound in powder form; and at least one metallic boride in powder form, the powder of vitreous compound and metallic boride being dispersed in the colloidal solution.

The colloidal aqueous solution may comprise at least one refractory oxide selected from the oxides of silicon, titanium, vanadium, yttrium, and zirconium, e.g. it may be a colloidal solution of silica.

The particles of refractory oxide in the colloidal solution are essentially of a size that is smaller than 200 nanometers (nm), preferably lying in the range 5 nm to 100 nm, and more preferably lying in the range 5 nm to 40 nm. Such nanometric particles can seal the porosity of the composite material at least in the vicinity of the surface on which the coating composition is applied.

It is preferable to use a colloidal solution that is basic. The basicity may be conferred by an additive, advantageously a stabilizer of the colloidal solution such as ammonia NH_3 or sodium oxide Na_2O . Thus, a good adhesion with the internal phosphate protection which is acidic is ensured, hence an anchoring of the coating in the surface porosity of the composite material.

The borosilicate type vitreous compound comprises the oxides B_2O_3 and SiO_2 . Other oxides may be present for adjusting the temperature at which the compound passes to the viscous state that makes self-healing possible. By

way of example, use is made of "Pyrex®" glass powder from the US supplier Corning or as provided by the British supplier Barloword Scientific (previously Bibby Sterilin), which glass has substantially the following composition (percentages by weight):

5	SiO ₂ :	80.60%
	B ₂ O ₃ :	12.60%
	Na ₂ O ₃ :	4.2%
	Al ₂ O ₃ :	2.25%
10	Cl:	0.1%
	CaO:	0.1%
	MgO:	0.05%
	Fe ₂ O ₃ :	0.05%
	

15 Other glasses could be used such as the borosilicate glasses referenced 823-01 to -05 from the US supplier Ferro, or the glasses sold by the German supplier Schott AG under the name "Duran" (preferably under the reference "8330"), "Suprax", or "Borofloat 40".

20 It will be noted that the refractory oxide of the colloidal solution may also contribute to the formation of glasses.

The metallic boride in powder form is at least one selected from the borides of titanium, vanadium, 25 zirconium, and hafnium. It is preferable to use TiB₂.

Typically, the composition of the coating comprises, by weight:

25% to 50%, and preferably 30% to 40%, of aqueous colloidal solution of refractory oxide with a 30 concentration of refractory oxide lying in the range 25%-50%;

5% to 20%, and preferably 10% to 15%, of vitreous compound that is essentially of the borosilicate type;

30% to 60%, and preferably 35% to 50%, of metallic 35 boride; and

the possible remaining being water.

The metallic boride is substantially present to constitute, through oxidation, a reservoir for the glass forming oxide B_2O_3 , the latter tending to volatilize when the temperature reaches $400^\circ C$ to $500^\circ C$.

5 The coating composition is applied (step 22) to the outside surface of the composite material part, in places where the impregnation composition has already been applied to form the internal protection. Application can be implemented by spraying on the composition or by means
10 of a brush. The quantity of the coating composition that is applied lies in the range about 10 milligrams per square centimeter (mg/cm^2) to $30 mg/cm^2$ before drying, and preferably in the range $12 mg/cm^2$ to $22 mg/cm^2$.

After the coating composition has been applied, heat
15 treatment is performed (step 24). Various different heat treatment temperatures can be implemented:

1) mere drying at a temperature lying in the range $80^\circ C$ to $100^\circ C$ for one or more hours (h), or while progressively raising the temperature up to $200^\circ C$ to
20 $250^\circ C$;

2) relatively short heat treatment in an oven under an oxidizing atmosphere (e.g. air) at a temperature of about $800^\circ C$ to $850^\circ C$ for a duration of a few minutes (min) to a few tens of minutes, preferably after drying
25 as in 1) above; or

3) heat treatment in an oven under a non-oxidizing atmosphere (e.g. nitrogen) at about $700^\circ C$, as for the internal protection.

Heat treatment 2) is preferred since it immediately
30 produces an outer protective layer having improved adhesion and hardness, and forming an effective protection barrier against the oxygen in the surrounding medium.

With mere drying (heat treatment 1)), it is the
35 subsequent exposure of the part to high temperatures in operation that produces an effect that is equivalent (but

delayed) to the effect of initial heat treatment at high temperature.

The quantity of coating composition applied is selected to obtain, after the heat treatment step, a coating thickness preferably between 50 μ m and 250 μ m and more preferably between 50 μ m and 100 μ m.

The composite material part as provided in this way both with internal protection and with external protection against oxidation is ready for use. While it is being used at high temperature in an oxidizing atmosphere, any loss of B₂O₃ by volatilization is compensated by the supply of B₂O₃ by oxidizing the metallic boride, thus enabling the self-healing properties to be maintained.

In a variant, it should be observed that it is possible to perform only a single heat treatment operation, with the coating composition being applied after the impregnation composition but without drying or heat-treating the impregnation composition.

Example 1

Samples of C/C composite material were made in the following manner:

fiber plies were formed by superposing three unidirectional sheets of carbon fibers making angles of $\pm 60^\circ$ relative to one another, with the sheets being bonded together by light needling;

the resulting fiber plies were superposed and the plies were bonded together by needling as they were being superposed so as to obtain a thickness of several centimeters;

circular preforms were cut out from the fiber plate as obtained in that way; and

the preforms were densified by a matrix of pyrolytic carbon formed by chemical vapor infiltration so as to obtain a relative density equal to about 1.73.

The resulting samples were impregnated with an aqueous solution containing 0.5% by weight of a wetting agent (surfactant) sold by the German supplier Hüls under the name "Marlophen 89". For this purpose, the samples
5 were immersed in a bath of said solution contained in a tank associated with an ultrasound generator for encouraging the solution to penetrate into the cores of the accessible pores in the composite material. The samples were subsequently dried at about 100°C for 5 h
10 leaving a film of wetting agent on the walls of the pores in the material.

Thereafter, an impregnation composition constituted by an aqueous solution having 50% by weight of aluminum dihydrogenphosphate $\text{Al}(\text{H}_2\text{PO}_4)_3$ was subsequently
15 impregnated by applying the solution to the outside surfaces of the samples in a quantity corresponding to 20 mg/cm².

After heat treatment in air for several hours by progressively raising the temperature up to about 350°C,
20 heat treatment was performed under nitrogen by raising the temperature to about 700°C and maintaining said temperature for about 1 h, so as to obtain samples provided with internal protection against oxidation based on phosphate anchored in the accessible internal pores of
25 the composite material.

The resulting samples provided with such internal protection were split into three groups:

- a) a first group of samples A that were left untouched;
- 30 b) a second group of samples B made from samples A and further provided with an external protective coating formed using a method in accordance with that described in US patent No. 6 740 408 and comprising:

- applying a coating composition to the outside
35 surfaces of the samples, the composition comprising approximately, by weight: 19% of silicone resin (sold by the German supplier Wacker-Chemie GmbH under the

reference "Wacker H62C"), 19% xylene (solvent of the resin), 13% by weight of "Pyrex®" glass powder, and 49% by weight of TiB_2 powder sold by the US supplier Alfa Aesar, the quantity of the applied coating composition
5 being about 17 mg/cm²; and

- heat treatment at about 220°C for about 2 h after raising the temperature slowly (at about 1.5°C/h) in order to cure the silicone resin; and

c) a third group of samples C constituted by samples
10 A further provided with an external protective coating made using a method in accordance with the present invention and comprising:

- applying an aqueous coating composition on the external surfaces of the samples C, the composition
15 comprising, approximately, by weight: 38.2 parts by weight of a 30% solution of colloidal silica in water (colloidal solution sold by the German supplier Chemische Fabrik Budenheim under the name "FFB33K"); 12.8 parts by weight of "Pyrex®" finely divided glass powder (grain
20 size essentially less than 50 micrometers (μm)); and 48.9 parts by weight of TiB_2 powder sold by the supplier Alfa Aesar, the quantity of applied coating composition being 17 mg/cm²; and

- heat treatment at about 90°C for about 2 h.

25 The samples A, B, and C were exposed to various oxidizing conditions using test protocols as defined in Table I below.

The table gives the relative weight losses that were measured (expressed in percentage relative to the weight
30 of the sample at the beginning of the test). Some of the tests were performed with the samples being "polluted" with potassium acetate (KAc) in an aqueous solution at 50 grams per liter (g/L), where KAc is a catalyst for oxidizing carbon and is commonly in substances for de-
35 icing airport runways.

Table I

Oxidation conditions	Reference oxidation conditions	KAc present	A	B	C
			20 ⁽¹⁾ mg/cm ²	20 ⁽¹⁾ mg/cm ² 17 ⁽²⁾ mg/cm ²	20 ⁽¹⁾ mg/cm ² 17 ⁽²⁾ mg/cm ²
5 cycles of 5 h at 650°C	p-650	No	4.6	1.4	-0.054
5 cycles of 30 min at 850°C	p-850	No	3.4	-0.2	-0.154
5 h at 650°C + 15 min at 1200°C + 2 cycles of 5 h at 650°C	p-1200	No	5.6	0.19	0.12
5 h at 650°C + 10 min at 1400°C + 2 cycles of 5 h at 650°C	p-1400	No	10.4	3.7	3.1
5 h at 650°C + KAc pollution + 2 cycles of 5 h at 650°C	p-650 KAc	Yes	6.6	2.7	2.05
5 h at 650°C + 15 min at 1200°C + KAc pollution + 2 cycles of 5 h at 650°C	p-1200 KAc	Yes	55.9	30.6	36.17

(1): quantity of the aluminum phosphate-based composition applied prior to heat treatment.

5 (2): quantity of the glass-based coating composition applied prior to heat treatment.

Negative values (i.e. increases in weight) are due to partial oxidation of TiB_2 giving the species TiO_2 and B_2O_3 , and they do not mask any loss in weight.

5 It can be seen that the results obtained with the samples C are considerably better than those obtained with the samples A, and in most cases better than the results obtained with the samples B, but without presenting the drawbacks involved with applying the external protection on those samples.

10 Two A and C samples were subjected to a process comprising:

a) aging at $650^\circ C$ in air for 30 h.

15 During the last 5 hours of the aging, the respective measured weight losses were 1.3% and 0% for the samples A and C.

The sample C was then subjected to steps b) and c) below:

20 b) a damaging process by immersion in water in an ultrasound vessel for about 15 minutes followed by cleaning using a metal brush; and

c) exposure to air at $650^\circ C$ for 5 h.

25 A relative weight loss of 0.43% was then measured after step c), showing additional improvement in comparison with the relative weight loss of 1.3% as measured on sample A after step a).

Two samples A and C were subjected to a process comprising:

a') the p-1400 oxidation protocol.

30 During the last 5 hours of that protocol, the respective weight losses as measured were 5.2% and 1.6% for the samples A and C.

The sample C was then subjected to the following steps b) and c):

35 b) a damaging process by immersion in water in an ultrasound vessel for about 15 minutes followed by cleaning using a metal brush; and

c) exposure to air at $650^\circ C$ for 5 h.

A relative weight loss of 2.4% was measured after step c), again showing an improvement compared with a relative weight loss of 5.2% as measured on a sample A after step a') on its own.

5 In spite of its severity, the damage applied to the samples C (step b)) leads to little loss in the effectiveness of the protection.

10 Those tests, simulating severe aging in a moist environment also show the very high resistance of the samples C when compared with the samples A, even though oxidizing TiB_2 gives B_2O_3 which is known to be soluble in water.

Example 2

15 A sample D of C/C composite material was provided with an external protective layer like the sample C of Example 1, but omitting the phosphate-based internal protection. Table II below shows the results obtained (relative weight losses) with the samples C and D under
20 two oxidation conditions.

Table II

Oxidation conditions	C	D
	20 ⁽¹⁾ mg/cm ²	-
	17 ⁽²⁾ mg/cm ²	17 ⁽²⁾ mg/cm ²
p-650	-0.054	0.731
p-650 KAc	2.05	6.95

25 The results obtained show the very considerable improvement in the protection by associating internal protection and external protection as compared with external protection on its own.

Examples 3, 4, and 5

30 A sample E was obtained by providing a sample A of Example 1 with external protection obtained by:

- applying an aqueous composition comprising 36.4 parts by weight of "FFB33K" colloidal silica at a concentration of 30%, 4.8 parts of water, 12.2 parts of "Pyrex" glass powder, and 46.6 parts of TiB_2 from the supplier Alfa Aesar the quantity applied being of about 17mg/cm²; and

- heat treatment at 90°C in air for 2 h.

A sample F was obtained like sample E except that the heat treatment was performed under nitrogen at 700°C for 1 h.

A sample G was obtained like sample E, except that the heat treatment was performed in air at 800°C for 15 min.

Table III below shows the results obtained (relative weight losses) after performing an oxidation test on the samples E, F, and G.

Table III

Oxidation conditions	E	F	G
p-650	0.264	1.4	0.256

Short heat treatment at 800°C in air is industrially preferable.

Example 6

A sample H was prepared like a sample A in Example 1, but using an aqueous solution of aluminum phosphate at a concentration of 48% as supplied by the German supplier Chemische Fabrik Budenheim and without proceeding with heat treatment after impregnation with that solution. Thereafter an aqueous solution was applied comprising 38 parts by weight of "FFB33K" colloidal silica at a concentration of 30%, 12.9 parts by weight of "Pyrex" glass powder, and 49.1 parts by weight of TiB_2 from the supplier Alfa Aesar.

Heat treatment was subsequently performed at about 700°C under nitrogen for about 1 h.

After oxidation in air at 650°C for 30 h, a relative weight loss of 2.5% was measured on the sample.

5 This example shows that it is possible to perform the heat treatment for internal protection and for external protection on a single occasion, but that the performance in terms of ability to withstand oxidation is significantly degraded.

10

Examples 7, 8, 9, 10, and 11

A sample I was obtained by providing a sample A of Example 1 with external protection obtained by:

15 - applying an aqueous composition comprising 38.2 parts by weight of "FFB33K" colloidal silica at a concentration of about 30% and stabilized by sodium by the presence of 0.4% to 0.5% by weight of Na₂O, 12.8 parts of "Pyrex" glass powder, and 48.9 parts of TiB₂ from the supplier Alfa Aesar;

20 - heat treatment at 90°C in air for 2 h.

A sample J was prepared like the sample I, but using an "FFB30K" colloidal silica from Chemische Fabrik Budenheim stabilized by the presence of about 0.3% by weight of Na₂O.

25 A sample K was prepared like the sample I, but using an "FFB34K" colloidal silica from Chemische Fabrik Budenheim stabilized by the presence of about 0.17% by weight of Na₂O.

30 A sample L was prepared like the sample I, but using an aqueous composition comprising 38.2 parts by weight of colloidal silica at a concentration of about 40% as supplied under the reference "Ludox AS 40" from the US supplier Grace Division and stabilized with ammonia, 12.8 parts of "Pyrex" glass powder, and 48.9 parts of TiB₂ from the supplier Alfa Aesar.

35

A sample M was prepared like the sample L, but using an aqueous composition comprising 30.8 parts by weight of

colloidal silica, 14.4 parts of "Pyrex" glass powder, and 54.8 parts of TiB_2 .

Table IV shows the results obtained (relative weight losses) under various conditions of oxidation for the samples C and I to M.

Table IV

Oxidation conditions	C	I	J	K	L	M
p-650	-0.054	-0.067	-0.111	0.059	-0.033	-0.024
p-850	-0.154	-0.214			-0.17	
p-1200	0.12	-0.11			0.46	
p-1400	3.1	3.52			3.50	
p-650 KAc	2.05	1.34			1.75	
p-1200 KAc	36.17	35.02	36.11	29.93	37.7	25.5

All of the colloidal silicas that were tested gave similar results.

Example 12

Samples N were obtained like sample F of example 4, the colloidal solution used being basic (stabilization by NH_3), the coating formed having a thickness of 90 μm .

Adhesion and hardness tests were carried out respectively on a sample N as initially obtained after heat treatment under nitrogen at 700°C during one hour, and on samples N after subsequent exposure in air to 650°C during 5h and to 850°C during 30h.

The adhesion test was a cross-cut test according to standard ISO/DIS 2409 allowing to assess the resistance of paint coatings to separation from substrates after cuts are made.

The hardness test was a scratch test according to standard ISO 1518, with measure of the minimum load to apply to cause a needle to penetrate into the coating.

Table V below summarizes the results obtained.

	Sample N in initial state	After 5h at 650°C	After 30h at 850°C
Adhesion	Class 3	Class 1	Class 2
Hardness (N)	3N	12N	12N

5 Good performances in adhesion and hardness can be noted after heat treatments in air which lead to glasses to be formed, said treatments reflecting the conditions to which aircraft brake disks in C/C composite material are exposed during their use.

10 Example 13

Samples A' and C' were made like the samples A and C, but applying the anti-oxidation protection on only one of the main circular faces and on the peripheral outline, while the other main face remained free from protection.

15 Friction tests were carried out on the samples A' and C' to measure firstly the coefficient of friction and secondly the effectiveness under braking conditions simulating an emergency landing. No significant difference was observed between the results obtained on a
20 sample A' and those obtained on a sample C'.

In addition, the samples C' were exposed at 30°C to relative humidity of 95% for durations of 1 day to 10 days and then the free face was examined using a scanning electron microscope provided with an EDX probe.
25 No chemical species coming from the anti-oxidation protection was observed, thus making it possible to conclude that there was total absence of any migration of such species to a friction surface of a brake disk protected against oxidation in accordance with the
30 invention by applying internal protection and external protection to its non-friction surfaces.

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

1. A method of providing protection against oxidation
5 for a part made of composite material containing carbon
and presenting open internal pores, the method
comprising the steps of:

- impregnating the part with a liquid impregnation
composition containing at least a phosphate compound,
10 via at least a fraction of the outside surface
of the part;

- applying a coating composition on said fraction
of the outside surface of the part, the coating
composition comprising a refractory oxide in an aqueous
15 solution of colloidal silica, at least one compound
essentially of a borosilicate in powder form and having
healing properties, and at least one boride selected
from the borides of titanium, vanadium, zirconium, and
hafnium in powder form; and

20 - applying heat treatment after applying the
coating composition, wherein the coating composition
comprises:

25 wt% to 50 wt% of the aqueous solution of
colloidal silica with a concentration of refractory
25 oxide lying in the range 25 wt% to 50 wt%;

5 wt% to 20 wt% of the at least one compound
essentially of a borosilicate in powder form;

30 wt% to 60 wt% of the at least one boride in
powder form, and 0 to 20 wt% of water.

30

2. The method according to claim 1 wherein the aqueous
solution of colloidal silica is basic.

3. The method according to claim 2 wherein the aqueous solution of colloidal silica is stabilized by a basic compound.

5 4. The method according to any one of claims 1 to 3, wherein the quantity of the coating composition that is applied is chosen to form a coating which, after heat treatment has a thickness lying in the range 50 μ m to 250 μ m.

10

5. The method according to claim 4, wherein the quantity of the coating composition that is applied is chosen to form a coating having a thickness lying in the range 50 μ m to 100 μ m.

15

6. The method according to any one of claims 1 to 3, wherein a first heat treatment is performed after impregnation with the impregnation composition, and a second heat treatment is performed after application of
20 the coating composition.

7. The method according to claim 6, wherein the second heat treatment is performed under an oxidizing atmosphere at a temperature of about 800°C to about
25 850°C for a relatively short duration of a few minutes to a few tens of minutes.

8. The method according to claim 1, wherein the at least one boride is a powder of titanium diboride (TiB₂).

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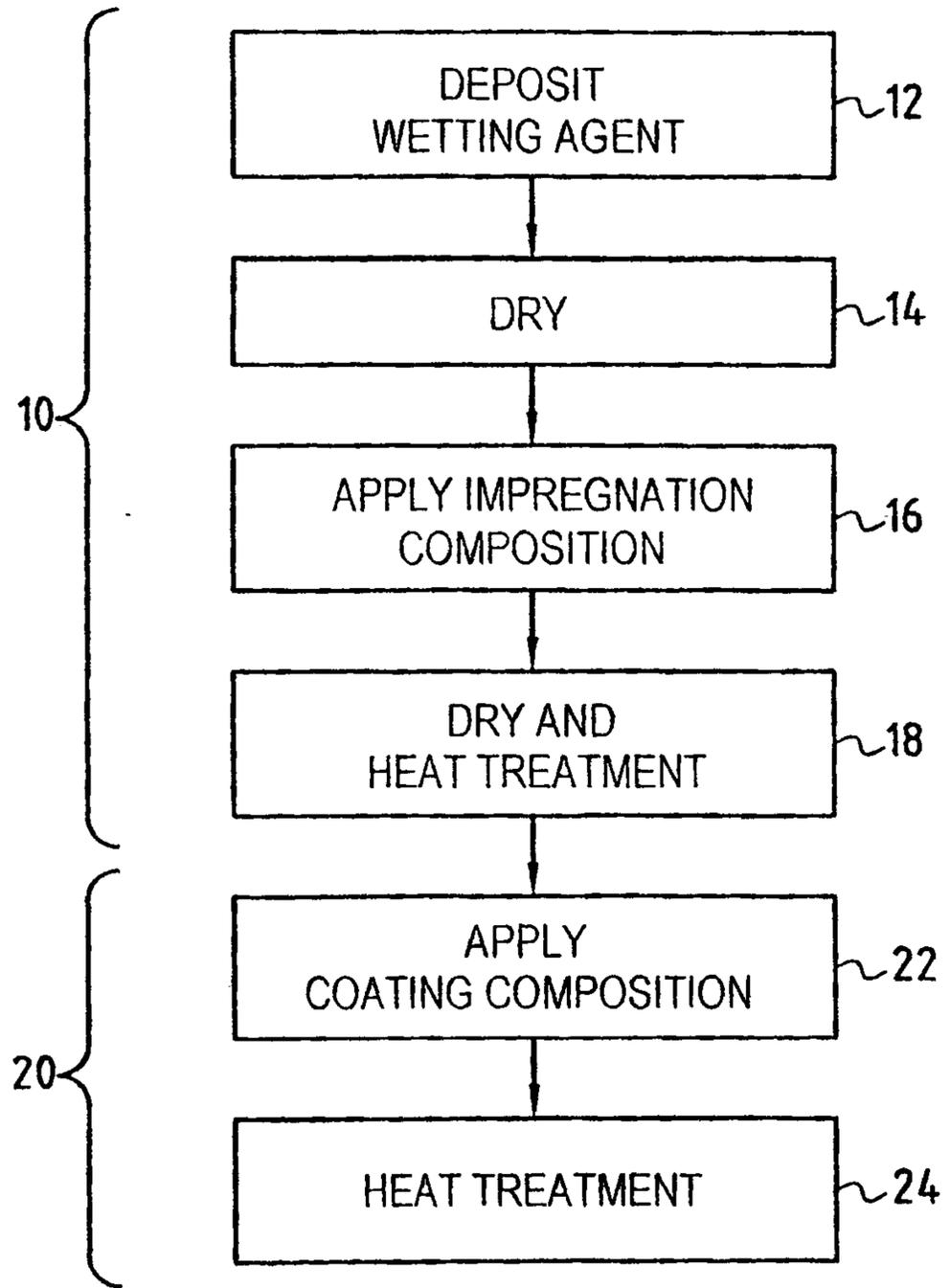


FIG.1

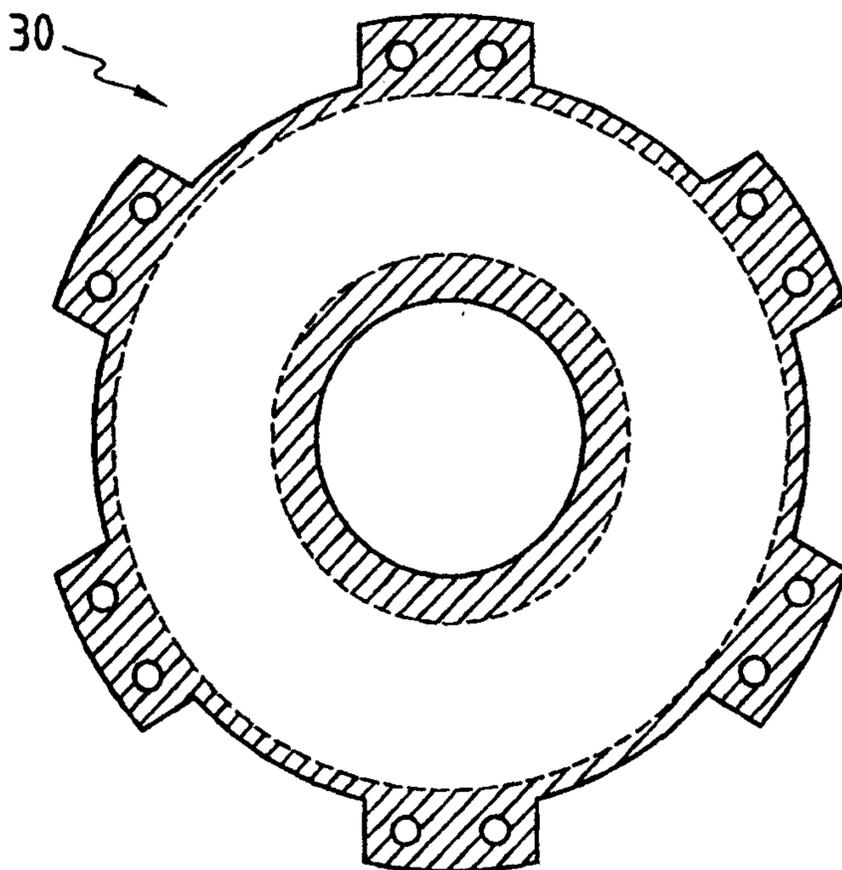
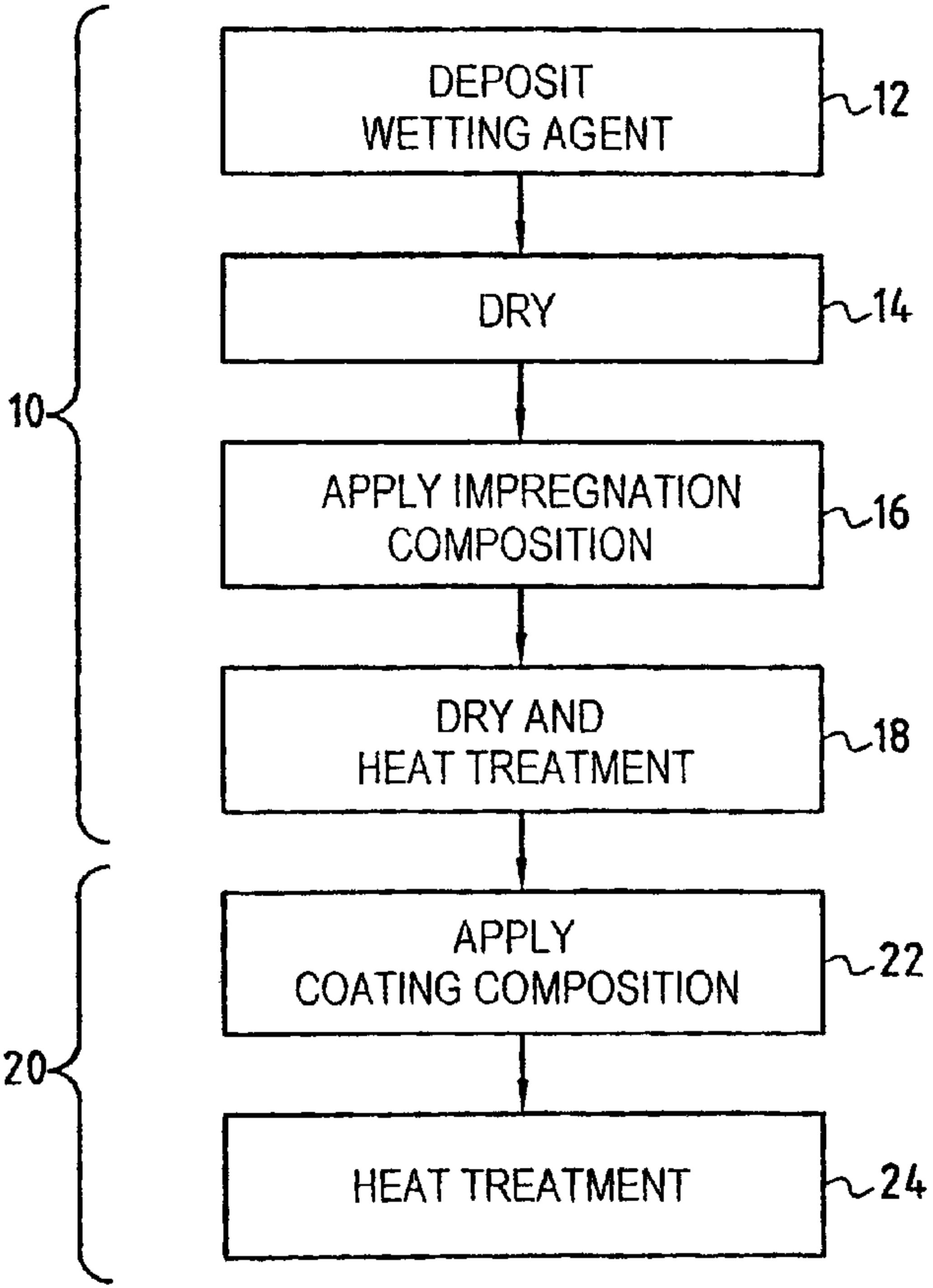


FIG.2



DEPOSIT
WETTING AGENT

12

DRY

14

APPLY IMPREGNATION
COMPOSITION

16

DRY AND
HEAT TREATMENT

18

APPLY
COATING COMPOSITION

22

HEAT TREATMENT

24

10

20