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ARTICLE COMPRISED OF A SOL-GEL COATING WITH A FUNCTIONAL DECOR, AND
METHOD FOR MANUFACTURING SUCH AN ARTICLE

5 The present invention generally relates to articles comprising a surface covered with a sol-gel coating with a functional decor. The present invention also relates to a method for manufacturing such articles.

The articles that the present invention relates to can in particular be cooking articles such as frying pans, pots, sauté pans, barbecue grills, soleplates of irons, or hair straightener plates.

10 The term "functional decor" means, in terms of the present invention, a decor that makes it possible to guide the user of the article in the usage thereof.

The term "sol-gel coating" means in terms of the present invention, a coating synthesised by the sol-gel process from a solution with a base of precursors in liquid phase, which are transformed into a solid by a set of chemical reactions (hydrolysis and
15 condensation), at low temperature. The coating thus obtained can be either organo-mineral, or entirely mineral.

The term "organo-mineral coating" means, in terms of the present invention, a coating of which the network is substantially inorganic, but which comprises organic groups, in particular due to the precursors used and the cooking temperature of the
20 coating.

The term "entirely mineral coating" means, in terms of the present invention, a coating formed from an entirely inorganic material, free of any organic group. Such a coating can also be obtained by the sol-gel process with a cooking temperature of at least 400°C, or from precursors of the tetraethoxy-silane (TEOS) type with a cooking
25 temperature which can be less than 400°C.

In the field of sol-gel coatings, in particular are known those obtained from metal alkoxides with a silicon (silane) base or an aluminium (aluminate) base.

These coatings are currently under substantial development in the field of cooking articles, and in particular as non-stick coatings covering the internal cooking surface.

30 These non-stick coatings, which are synthesised by the sol-gel process from precursors of the metal polyalkoxylate type, have a hybrid network, generally of silica with grafted alkyl groups. With respect to conventional non-stick coatings for cooking articles with a polytetrafluoroethylene (PTFE) base, this type of coating obtained by the sol-gel process has, as a main advantage, a very good resistance to temperatures greater
35 than 300°C.

A formulation of this type of coating is described in international application WO 2008/010639. This is, in particular, a coating formed by the sol-gel process from a composition with a silane base, with this coating being applied on a support made of anodised aluminium intended to be used as a cooking article.

Moreover, the applicant has also developed a coating of this type intended for cooking articles. Thus, international application WO 2008/142327 and European application EP 2 139 964, belonging to the applicant, describe a coating formed by the sol-gel process from a composition with a base of at least one metal alkoxide and a colloidal metal oxide, wherein is added a very small quantity of silicone oil. The coating thus formed not only resists high temperatures, but it is also capable of withstanding passing for several minutes in the flame of a Bunsen burner (of which the temperature is greater than 600°C) and to then quickly return to the hydrophobic character thereof.

International patent application WO 2007/104258 and European application EP 1 835 002n belonging to the company CERASOL HONG KONG LDT specialised in the research and development of ceramic coatings for domestic and industrial applications, describe the formulation and method for manufacturing a non-stick coating that resists abrasion, and a hardness and a resistance to wear that are improved with respect to a PTFE coating. This is a two-layer coating formed from a primary compound of colloidal silica, of organoalkoxysilanes with possibly a polydimethylsiloxane (PDMS), and with a transparent finishing layer comprised of colloidal silica of organoalkoxysilanes of which a fluoroalkoxysilane in order to provide the anti-adhesiveness and possibly a PDMS.

Finally, patent application CN 101502378 describes, in detail, the formulation of a coating for cooking articles that make it possible to reduce, even suppress the oxidation of edible oils. This is a coating formed by the sol-gel process from a composition with a methyltrimethoxysilane (MTMS) or methyltriethoxysilane (MTES) base and a dispersion of colloidal alumina, loaded with different inorganic fillers of which a nano silver powder that makes it possible to stop the oxidation mechanism of oils.

None of these coatings of the sol-gel type known from the prior art is provided with a functional indicator, i.e. an indicator that makes it possible to accompany and guide the user of the article on which the coating in question is deposited.

The present invention aims to propose to the consumer an article that comprises a coating synthesised by the sol-gel process, provided with a functional decor that makes it possible to guide the consumer in the use thereof.

More particularly, the present invention aims for an article comprising a support having two opposite faces, and a sol-gel coating covering at least one of the faces of said support, said sol-gel coating being in the form of a continuous film of a material comprising a matrix formed from at least one metal polyalkoxylate and at least 5% by weight with respect to the total weight of the coating of at least one colloidal metal oxide dispersed in said matrix. Said sol-gel coating is coated with a functional decor which is presented in the form of at least one non-continuous layer comprising at least one optically non-transparent chemical substance, and of which the composition is selected from the group of decor compositions free of thermostable binder. The functional decor is covered with a continuous transparent finishing layer, which comprises, as a binder, a sol-gel material comprising a matrix formed by at least one metal polyalkoxylate and at least 5% by weight with respect to the total weight of the coating of at least one colloidal metal oxide dispersed in the matrix.

The transparent finishing layer is used to protect the decor of the abrasion (while still leaving a visibility of the underlying decor) and provides all of the coating (i.e. the sol-gel coating, the decor and the finishing layer) with the non-stick properties thereof.

In the scope of the present invention, the functional indicator is a differentiating element, active or passive, that has a colour and/or a shine that is different from the sol-gel coating at least at a given temperature.

In the case of a passive functional indicator, this or these difference(s) is/are thermostable (i.e. do not change when the temperature of the article changes), which can, for example, consist of a graduation, or a mark that makes it possible to visually guide the user for positioning the food at the centre of the article (in the case of a cooking article).

In the case of an active functional indicator, this (or these) difference(s) is/are thermochromic (i.e. changing when the temperature of the article changes), which can therefore indicate to the user of the article the temperature reached by the coating in the process of use. Thus, a thermochromic functional indicator is of interest in the case of a cooking article, where good control of the temperature during the cooking of food is required for sanitary and taste reasons (for example, for searing a steak on a grill or in a frying pan), and for limiting one-off overheating which weaken the coating of the cooking article. In the case of a hair straightener, a thermochromic functional indicator makes it possible for the user to know the optimum temperature of use of the straightener. Finally, in the case of an iron, a thermochromic functional indicator makes it possible to prevent, for example, any risk of burning with the hot soleplate (in particular when the iron has

reached the operating temperature thereof and the lighted indicator of the thermostat goes out).

In terms of optically non-transparent chemical substances that can be used in the decor layer according to the invention, mention can thus be made of thermostable pigments, thermochromic pigments, flakes, and mixtures thereof.

A passive functional indicator in terms of the present invention will only comprise pigments or thermostable flakes in terms of optically non-transparent chemical substances.

On the other hand, an active functional indicator in terms of the present invention will necessarily comprise, in terms of optically non-transparent chemical substances, a thermochromic pigment composition, with at least one thermochromic pigment, which is preferably semiconducting (SC).

Preferably, the decor can comprise at least two partially superimposed non-continuous layers.

According to an embodiment of the invention, the internal surface of the support is covered, at least partially by a non-continuous decor comprising a plurality of patterns, which can be divided into two categories:

- patterns that comprise a thermochromic pigment that darkens with the rise in temperature (for example, ferric oxide), and
- patterns that comprise a thermochromic pigment that lighten with the temperature (for example, a pigment mixture formed from perylene red and from a food-grade black pigment such as FA1120 from FERRO).

According to another embodiment of the invention, this thermochromic pigment composition can comprise:

o composite pigment grains with a core-envelope structure, the diameter of which is between 20nm and 25000nm, and which each comprise:

- a core comprising an SC pigment that is thermochromic and lipid-sensitive under heat (i.e. likely to be broken down hot in contact with an oil or with a fat), and

- a solid, transparent and continuous envelope formed by a mineral material (which is preferably a silica shell) or a hybrid organo-mineral material, and

o optionally at least one thermostable pigment, located inside or outside the composite pigment grains, the thermostable pigment being such as defined above.

In terms of a metal polyalkoxylate that can be used as a binder in the coating as well as in the finishing layer, mention can be made, in particular, of polyalkoxysilanes, aluminates, titanates, zirconates, vanadates, borates and the mixtures thereof.

In terms of a colloidal metal oxide that can be used in the coating as well as in the finishing layer, mention can be made in particular of silica, alumina, cerium oxide, zinc oxide, vanadium oxide and zirconium oxide. The preferred colloidal metal oxides are silica and alumina.

As the decor according to the invention is free from thermostable binder, the adding of formulation additives can be necessary to adapt the properties of the composition to the method of application. Thus, for applications by screen printing or pad printing, the presence of at least one thickener is required in the composition of the decor layer(s), this thickener can be of an organic (urethane base, acrylic base, cellulose base, etc.) or inorganic (pyrogenic silica, Laponite®, etc.) nature. Other methods of applying the decor are possible, in particular by spraying, screen, roller, soaking, brush, by ink jet, etc. The compatibility of a decor without a binder with the adjacent layer or layers (here, the layer of sol-gel coating and, where applicable, the finishing layer) is perfect: absence of any problem concerning wettability during the application of the surface layer on the decor and absence of any problem of cleavage of the layers after cooking. Furthermore, the composition of a layer of decor without binder can easily be adapted to various methods of application, while remaining stable over time.

Different types of articles, according to the invention, different forms and manufactured in different materials can be considered.

Thus, the support can be made of a material selected from metals, wood, glass, ceramics and plastics.

Preferably, the support will be a metal support made of anodised or non-anodised aluminium, or of polished, brushed or microbeaded aluminium, sanded, chemically treated or of polished, brushed or microbeaded stainless steel, or of cast iron; or of hammered or polished copper.

With regards to the form, the support must have the final form of the article, because it cannot be stamped after the deposition of the sol-gel coating.

In the cooking field, it is moreover possible to consider different forms of support, and in particular cooking articles as such, intended or not for the cooking of food, with:

- a first of the opposite faces is an internal concave face intended to be arranged on the side of the food that may be placed inside the article, and
- a second of the opposite faces is an external convex face intended to be arranged on the side of a heat source.

By way of non-limiting examples of cooking articles, according to the present invention, mention will be made in particular of cooking articles such as pots and pans,

woks and sauté pans, crepe pans, grills, moulds and plates for pastries, barbecue plates and grills.

Other types of supports which are not limited only to the cooking field can also be considered. Thus, it is also possible to consider as articles, according to the invention,
5 household electrical appliances, or components made of plastic for motor vehicles or bottling.

The present invention further aims for a method of manufacturing an article according to the invention, comprising the following series of steps:

a) providing a formed metal support comprising two opposite faces, then

10 b) producing a sol-gel coating on at least one of the faces of said support, which comprises the following series of steps:

- b1) preparing a sol-gel composition SG comprising at least one colloidal metal oxide and at least one metal alkoxide precursor;

- b2) applying, on all or part of at least one of the faces of said support, at least
15 one layer of the sol-gel composition SG having a thickness of at least 5µm; then

d) cooking the article to obtain a sol-gel coating having a thickness of at least 1µm, said method being characterized in that it further comprises, prior to the cooking step d), a step c) of producing a functional decor comprising the application, on at least one part of the sol-gel coating, of at least one layer with a decor composition comprising
20 at least one optically non-transparent chemical substance to form a decor, said decor composition having a minimum viscosity of 1.5Pa.s measured at room temperature and for a shear rate of between 1 and 1000s⁻¹.

The measurement of the viscosity can be taken using a viscosimeter (for example, the one commercialised by the company BROOKFIELD) or a rheometer (for example, the
25 one commercialised by the company GEMINI).

The cooking of the sol-gel coating and finishing layers is therefore carried out simultaneously.

The metal alkoxide is such as defined above. This is preferably a colloidal metal oxide selected from among colloidal silica and/or colloidal alumina.

30 Use is given preferably as a precursor a metal alkoxide selected from among the group comprising:

- precursors having the general formula $M_1 (OR_1)_n$,
- precursors having the general formula $M_2 (OR_2)_{(n-1)}R_2'$, and
- precursors having the general formula $M_3 (OR_3)_{(n-2)}R_3'^2$, with:

35 R_1 , R_2 , R_3 or R_3' designating an alkyl group,

R_2' designating an alkyl group or a phenyl group,
n being a whole number corresponding to the maximum valency of the metals M_1 ,
 M_2 or M_3 ,

M_1 , M_2 or M_3 designating a metal selected from among Si, Zr, Ti, Sn, Al, Ce, V, Nb,
Hf, Mg or Ln.

Advantageously, the metal alkoxide of the solution SG is an alkoxysilane.

In terms of alkoxysilanes that can be used in the solution SG of the method of the
invention, it is possible in particular to mention methyltrimethoxysilane (MTMS),
tetraethoxysilane (TEOS), methyltriethoxysilane (MTES), dimethyldimethoxysilane, and
mixtures thereof.

Preferably, the alkoxysilanes MTES and TEOS will be used, because they have
the advantage of not containing any methoxy groups. Indeed, the hydrolysis of methoxy
leads to the formation of methanol in the sol-gel formulation, which given the toxic
classification thereof, it requires additional precautions during application. On the contrary,
the hydrolysis of ethoxy groups generates only ethanol which has a more favourable
classification and therefore prescriptions for use that are less constraining for the sol-gel
coating.

Advantageously, the method according to the invention can further comprise
between the step c) of producing the functional decor and the cooking d) of the article, a
step c') of applying, on said decor, a continuous transparent finishing layer comprising:

- the preparation of a transparent sol-gel composition SG' comprising at least one
colloidal metal oxide and at least one metal oxide precursor; then
- the application, on the decor and the parts of the sol-gel coating that may not be
covered by the decor, of at least one layer of the sol-gel composition SG' having a
thickness of at least $1\mu\text{m}$ in the wet state.

Advantageously, the decor can comprise, as a thickener, an anionic polyelectrolyte
in an amount of 2% to 20% by weight with respect to the total weight of the decor.

The invention is shown in more detail in the following examples. In the examples,
unless mentioned otherwise, all of the percentages and portions are expressed by weight.

EXAMPLES

Products

Functional decor layer

Thermostable pigments

- titanium dioxide (white colour) (RN56 grade from Kronos)
- polysulphide sodium aluminosilicate of Pacific blue colour (CM13 grade from Holliday Pigments)

5 • or any other pigment that can resist a temperature greater than or equal to 200°C

Thermochromic pigments

- Ferric oxide Fe_2O_3 commercialised by the company Bayer under the name Bayferrox

10 • Perylene red, associated with a food-grade thermostable black pigment (FA1220 from Ferro)

Flakes: Iriodin 100 flakes from Merck

Thickener: methacrylic acid and acrylic ester copolymer

Solvent: propylene glycol

Base and finishing coating layers

15 • colloidal silica in the form of a 30% aqueous solution of silica, commercialised by the company Clariant under the commercial name Klebosol

- Isopropanol

 • food-grade black pigments commercialised by the company FERRO under the commercial name FA1220

20 • sol-gel polymerisation precursor: methyltriethoxysilane MTES

- organic acid: acetic acid

EXAMPLE 1: Production of examples of cooking articles according to the invention

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A cooking recipient is produced, according to the invention, in the manner described below, in reference to the appended figures given by way of non-limiting examples:

30 - figure 1 is a cross-sectional view of a comparative cooking recipient provided with a thermochromic decor arranged on the sol-gel coating, without a finishing layer.

 - figure 2 is a cross-sectional view of a first example of a cooking recipient according to the invention, provided with a thermochromic decor arranged on the sol-gel coating, itself coated with a finishing layer,

35 - figure 3 is a top view of the comparative recipient of figure 1 and of the recipient according to the invention shown in figure 2,

- figure 4 is a top view of a second example of a cooking recipient according to the invention provided with a thermostable decor in the form of a dot in the shape of a disc arranged at the centre of the internal surface of the recipient,

- figure 5 is a top view of a third example of a cooking recipient according to the invention provided with a thermostable decor in the form of concentric circles.

The identical elements shown in figures 1 to 5 are identified by identical numerical references.

Figures 1 to 5 show a comparative cooking article (figure 1) and, as an example of a cooking article according to the invention (figures 2 to 5), a frying pan 1 comprising a metal support 2 in the form of a hollow canopy provided with a gripping handle 6, the support 2 having an internal surface 21 intended to be heated and to receive food for the purpose of cooking it, and an outer surface intended to be arranged on a heat source.

On the comparative cooking article shown in figure 1, the internal surface 21, which was at least degreased and made free of dust beforehand, is covered with a coating 3 of the sol-gel type, according to the production method described in example 3. Typically, it can comprise food-grade black pigments such as FA1220.

To favour the sticking of the coating 3 of the sol-gel type on the internal surface 21 of the support 2, this is treated beforehand (for example, by sandblasting) so as to increase the specific surface thereof.

The sol-gel coating 3 is covered at least partially with a non-continuous decor that comprises a plurality of patterns 41, 42, which are divided into two categories as shown in figure 3:

- patterns 41 which comprise ferric oxide Fe_2O_3 , which is a thermochromic pigment that darkens with the rise in temperature, and

- patterns 42 which comprise a thermochromic pigment mixture that lightens with the temperature formed of perylene red and of FA1220

The decor with the two categories of different patterns 41, 42 thereof is applied via pad printing, according to the embodiment of the layer of decor described in example 2.

The first alternative of the cooking article according to the invention, which is shown in figure 2 (as well as in figure 3 for the distribution of the patterns), is differentiated from the comparative cooking article (shown in figure 1) in that a transparent finishing layer 5 is applied on the decor and the parts of coating 3 of the sol-gel type that are not covered with the patterns 41, 42 of the decor, according to the manufacturing method described in example 4.

Non-stick performance

For the comparative coating shown in figure 1: **acceptable** because it is easy to remove a cooked egg on the comparative coating using a spatula

For the coating according to the invention shown in figure 2: **clearly improved** with respect to those obtained with the comparative coating shown in figure 1 because an egg cooked on such a coating according to the invention slides with a simple movement of the article.

Resistance to wear

For the comparative coating shown in figure 1: **acceptable** because the comparative coating can be subjected to 500 passes of a scouring pad without deteriorating the decor (resistance to wear).

For the coating according to the invention shown in figure 2: **clearly improved** with respect to those obtained with the comparative coating shown in figure 1 because the coating according to the invention can be subjected to 5000 passes of a scouring pad without deteriorating the decor.

On a second alternative cooking article according to the invention shown in figure 4, the decor is comprised of a central dot 43 arranged at the centre of the article 1. This pastille 43 comprises a thermostable pigment, for example titanium dioxide for a white colour (of RN56 grade from Kronos) or a Pacific blue polysulphide sodium aluminosilicate (CM13 grade from Holliday Pigments). Such a pattern 43 can make it possible to identify a cooking article (colour code by type of use: for example, a pattern 43 of blue colour for a specific use for cooking fish, a pattern 43 of red colour for a specific use for cooking meats, a pattern 43 of green colour for a specific use for cooking vegetables, etc.).

On a third alternative of a cooking article according to the invention shown in figure 5, the decor is formed of concentric circles 44 comprising flakes (for example, Iriodin 100 from Merck). Such a pattern 44 makes it possible to assist the consumer in correctly positioning the food that the consumer wants to cook on the article 1.

EXAMPLE 2: production of a decor layer

Two pigment pastes are prepared beforehand as follows:

- the first pigment paste is obtained by dispersing 50g of ferric oxide Fe_2O_3 , in 100g of water, while

- the second pigment paste is obtained by dispersing 35g of perylene red and 15g of FA1220 in 100g of water.

The composition (or formula) of each one of the patterns 41, 42 differs only by the nature of the pigments used, and therefore by the pigment paste used. Each composition therefore comprises a pigment paste, diluted with water and a mixture of heavier solvents such as propylene glycol to control the drying of the formula. Two dispersions are therefore obtained, which are each then sufficiently thickened using an anionic polyelectrolyte (methacrylic acid and acrylic ester copolymer) to have a rheology that is suitable for an application via pad printing.

The two thickened compositions thus obtained (one with a base of the first pigment paste, and the other with a base of the second pigment paste) are applied, in the form of contiguous patterns in at least one layer on the coating 3 of the sol-gel type, according to the comparative cooking article of figure 1 and with the first and second alternative cooking articles according to the invention shown in figures 2 and 3.

In the case of an application in several layers of these thickened compositions, each layer is dried before the application of the following layer.

These two thickened compositions are applied in contiguous zones to improve the legibility of the curved zone (i.e. greater facility for the reader in understanding the indication given by the thermochromic patterns 41, 42).

EXAMPLE 3: production of the layer 3 of sol-gel coating

A sol-gel composition is prepared in the form of a bi-component comprising a part A and a part B:

- the part A comprises a dispersion of colloidal silica, water in order to make it possible for the hydrolysis of the metal precursors of the part B, isopropanol in order to make it possible for good compatibility of the parts A and B and food-grade black pigments.

- the part B comprises, as a sol-gel precursor, methyl triethoxysilane, which makes it possible for the formation of the matrix of the coating by rejecting only the ethanol (which is a non-toxic volatile organic compound (VOC), contrary to methyltrimethoxysilane which leads to the formation of methanol, which is a toxic VOC), as well as acetic acid which makes it possible to catalyse the sol-gel reaction.

These two parts A and B can be stored for more than 6 months in this separated form.

Then, the parts A and B are combined together in a mixer to create an intimate mixture and make it possible for the initiation of the hydrolysis reaction. It is then necessary to leave the mixture to mature for at least 24 hours before application per se, so as to allow the hydrolysis and condensation reactions to sufficiently progress. The lifespan in the pot of the mixture is at least 72 hours.

Then, the mixture is filtered on a stainless steel grid with orifices of 40 microns in diameter before being applied, with a pneumatic gun, in at least one layer of thickness of 5 to 50 microns directly and integrally on the internal surface 21 of the support 2 according to the comparative cooking article of figure 1 and with the first and second alternative embodiments (respectively shown in figures 2 and 3).

In the case of an application in several layers, each layer is dried before the application of the following layer.

A layer 3 of coating is obtained, which is then subjected to cooking at 250°C for 15 minutes.

EXAMPLE 4: production of the finishing layer 5

A finishing layer 5 is produced in the same way as the layer of sol-gel coating 3, with the only difference being that it must remain transparent.

The formulation of the parts A' and B' (corresponding respectively to the parts A and B of example 3), the operating method and the application are identical to those described in example 3.

The methyl groups of the matrix of the coating with a methyl triethoxysilane base provide this layer 5 with non-stick properties. These properties can be improved by the adding of silicone oil in the finishing layer 5, as described in European patent application EP 2 139 964.

Once all of the layers are applied and dried, the article 1 is baked at 250°C for 15 minutes. The cooking of the coating 3 of the sol-gel type and that of the finishing layer 5 must be carried out simultaneously.

Of course, the invention is not limited to the examples that have just been described (mainly cooking articles) and it is possible to consider other types of heating articles (for example, soleplates of irons, barbecue grill plates, etc.) without moving away from the scope of the invention.

Patentkrav

- 1.** Artikel (1) omfattende et substrat (2) med to modstående flader (21), og en sol-gel-belægning (3), der dækker mindst en af substratets (2) flader (21),
5 idet sol-gel-belægningen (3) er i form af en kontinuerlig film af et materiale omfattende en matrix dannet af mindst et metaltpolyalkoxylat og mindst 5 vægtprocent i forhold til belægningens (3) samlede vægt af mindst et kolloidalt metaloxid dispergeret i matrixen, og
idet sol-gel-belægningen (3) er belagt med en funktionel udsmykning, der er i
10 form af mindst et ikke-kontinuerligt lag omfattende mindst et optisk ikke-transparent kemisk stof, og hvis sammensætning er valgt blandt gruppen af udsmykningssammensætninger, der er fri for termostabilt bindemiddel,
kendetegnet ved, at udsmykningen er belagt med et kontinuerligt transparent dæklag (5), der som bindemiddel omfatter et sol-gel-materiale omfattende en
15 matrix dannet af mindst et metaltpolyalkoxylat og mindst 5 vægtprocent i forhold til belægningens samlede vægt af mindst et kolloidalt metaloxid dispergeret i matrixen.
- 2.** Artikel (1) ifølge krav 1, **kendetegnet ved, at** udsmykningen omfatter mindst
20 to delvist overlejrede, ikke-kontinuerlige lag.
- 3.** Artikel (1) ifølge et hvilket som helst af krav 1 og 2, **kendetegnet ved, at** udsmykningen som fortykningsmiddel endvidere omfatter en anionisk polyelektrolyt i en mængde på 2 til 20 vægtprocent i forhold til udsmykningens
25 samlede vægt.
- 4.** Artikel (1) ifølge et hvilket som helst af kravene 1 til 3, **kendetegnet ved, at** det optisk ikke-transparente kemiske stof er valgt blandt termostabile pigmenter, termokrome pigmenter, pailletter og blandinger deraf.
30
- 5.** Artikel (1) ifølge krav 4, **kendetegnet ved, at** udsmykningen som optisk ikke-transparent kemisk stof omfatter en termokrom pigmentsammensætning med mindst et termokromt pigment, hvilket fortrinsvis er en halvleder (SC).

6. Artikel (1) ifølge krav 5, **kendetegnet ved, at** den termokrome pigmentsammensætning omfatter:

- kompositpigmentkorn med en kerne-kappe-struktur, hvis diameter er på mellem 20 nm og 25000 nm, og som hver omfatter:

- 5 ▪ en kerne omfattende mindst et termokromt SC-pigment, som er lipid-sensitivt under varme, og
- en fast, transparent og kontinuerlig kappe, som består af et mineralsk materiale eller et organomineralsk hybridmateriale.

10 7. Artikel (1) ifølge krav 6, **kendetegnet ved, at** den termokrome pigmentsammensætning endvidere omfatter mindst et termostabilt pigment, som befinder sig inde i eller uden for kompositpigmentkornene.

8. Artikel (1) ifølge krav 6 eller 7, **kendetegnet ved, at**
15 kompositpigmentkornenes kappe er en silicaskal.

9. Artikel (1) ifølge et hvilket som helst af kravene 1 til 8, **kendetegnet ved, at** den er en madlavningsartikel (1), hvor en af de modstående flader er en indvendig konkav flade (21) beregnet til være anbragt på den side, hvor
20 fødevarerne kan blive indført i artiklen (1), og en anden af de modstående flader er en udvendig konkav flade beregnet til at blive anbragt mod en varmekilde.

10. Artikel (1) ifølge et hvilket som helst af kravene 1 til 9, **kendetegnet ved, at** substratet (2) er fremstillet af et materiale valgt blandt metaller, træ, glas,
25 keramik og plastmaterialer.

11. Artikel (1) ifølge krav 10, **kendetegnet ved, at** substratet er en metalholder fremstillet af anodiseret eller ikke-anodiseret aluminium; eller af poleret, børstet eller mikrokugleblæst, sandblæst, kemisk behandlet aluminium; eller af poleret,
30 børstet eller mikrokugleblæst rustfrit stål; eller af støbejern; eller af hamret eller poleret kobber.

12. Fremgangsmåde til fremstilling af en artikel (1) som defineret ifølge et hvilket som helst af kravene 1 til 11, omfattende følgende successive trin:

a) tilvejebringelse af et formet metalsubstat (2) med to modstående flader (21), derefter

b) tilvejebringelse af en sol-gel-belægning (3) på mindst en af substratets (2) flader (21), hvilket omfatter de følgende successive trin:

- 5 • b1) fremstilling af en sol-gel-sammensætning SG omfattende mindst et kolloidalt metaloxid og mindst en precursor af typen metalalkoxid;
- b2) påføring, på hele eller en del af mindst en af substratets (2) flader (21), af mindst et lag af sol-gel-sammensætningen SG med
- 10 en tykkelse på mindst 5 μm ; derefter

d) brænding af artiklen (1) for at opnå en sol-gel-belægning (3) med en tykkelse på mindst 1 μm ,

hvilken fremgangsmåde er **kendetegnet ved, at** den forud for brændingstrinnet

d) endvidere omfatter et trin c) til frembringelse af en funktionel udsmykning

- 15 omfattende påføring på i det mindste en del af sol-gel-belægningen (3) af mindst et lag af udsmykningssammensætning omfattende mindst et optisk ikke-transparent kemisk stof for at danne en udsmykning, hvilken udsmykningssammensætning har en minimumsviskositet på 1,5 Pa.s målt ved omgivelsestemperatur og ved en forskydnings hastighed på mellem 1 og 1000 s^{-1} .

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13. Fremgangsmåde ifølge krav 12, **kendetegnet ved, at** den mellem trin c) til frembringelse af den funktionelle udsmykning og brændingen d) af artiklen (1) endvidere omfatter et trin c') til påføring, på udsmykningen, af et kontinuerligt transparent dæklag (5), omfattende:

- 25 - fremstilling af en transparent sol-gel-sammensætning SG' omfattende mindst et kolloidalt metalalkoxid og mindst en metaloxidprecursor; derefter
- påføring, på udsmykningen og de dele af sol-gel-belægningen (3), der eventuelt ikke dækkes af udsmykningen, af mindst et lag af sol-gel-sammensætningen SG' med en tykkelse på mindst 1 μm i våd tilstand.

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14. Fremgangsmåde ifølge krav 12 eller 13, **kendetegnet ved, at** udsmykningen er fri for termostabilt bindemiddel og, som fortykningsmiddel, omfatter en anionisk polyelektrolyt i en mængde på 2 til 20 vægtprocent i forhold til udsmykningens samlede vægt.

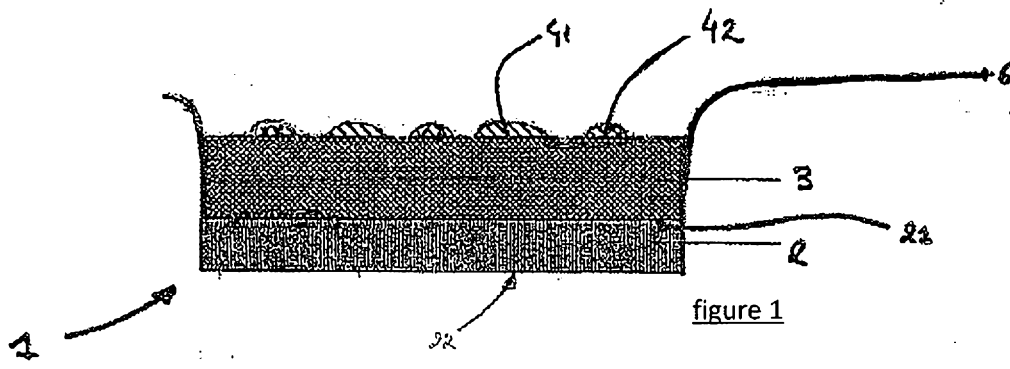


figure 1

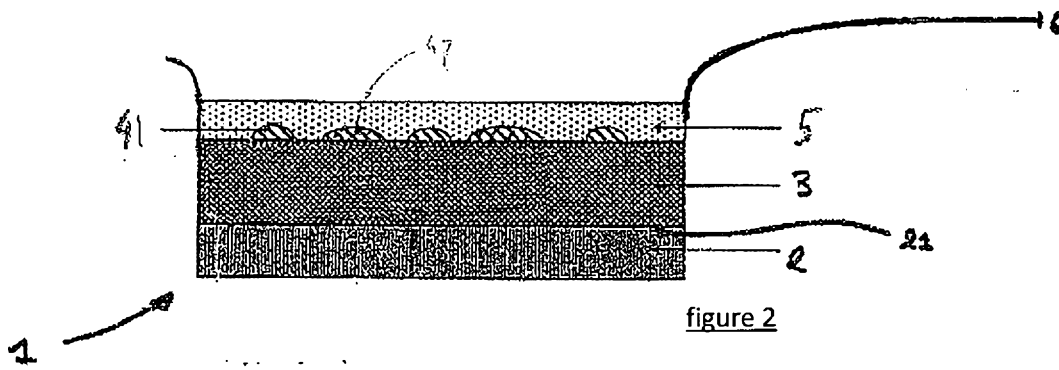


figure 2

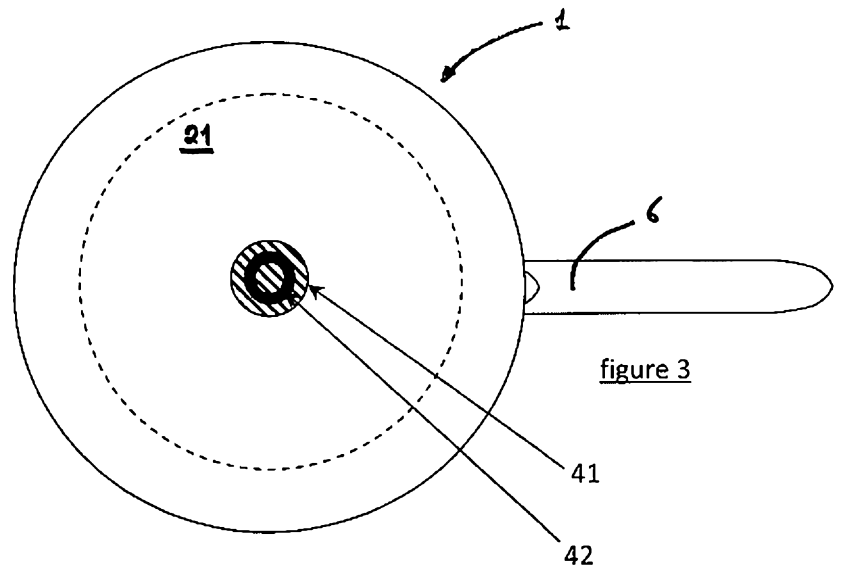


figure 3

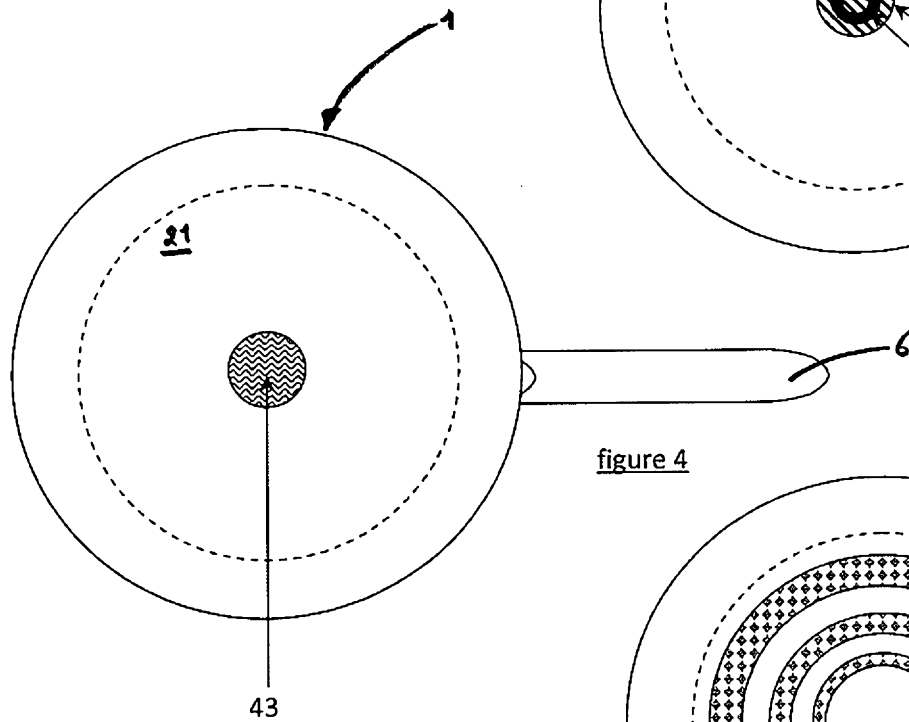


figure 4

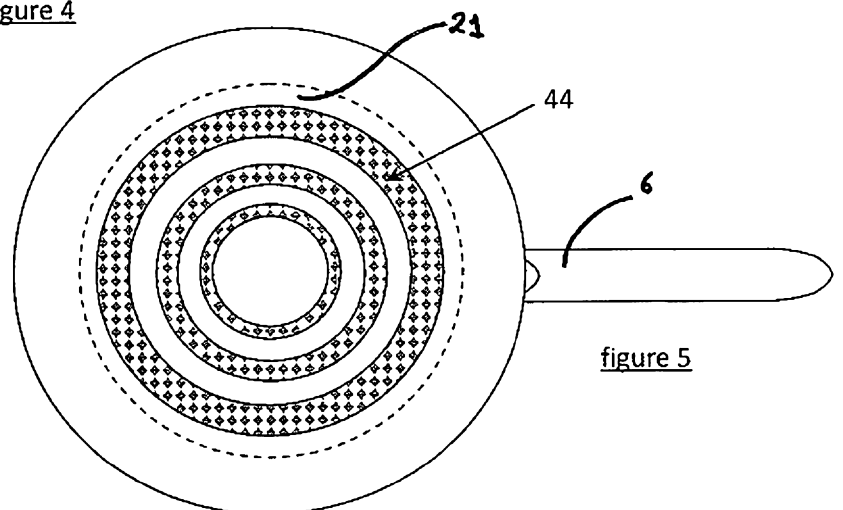


figure 5