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(54) NON-STICK COATING COMPOSITIONS

- (71) We, S. A. TEFAL, a French Company of Rumilly (Haute Savoie), France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to a non-stick coating composition containing a fluorocarbon resin, for example for coating metal surfaces, such as aluminium discs.
- The invention also relates to the process for the production of such a non-stick coating, and it also relates, under the heading of a novel industrial product, to the resulting manufactured article.
- Fluorocarbon polymer based coatings as non-stick coatings in kitchen utensils have developed rapidly since 1956. At the present time they are in widespread use since the process described in French Patent No. 1,120,749 provided a reliable fixing of such coatings on various metals, *inter alia* aluminium and its alloys.
- In this process, the metal surface is subjected to chemical attack to produce a porous keying layer thereon. The fluorocarbon polymer can then be fixed in the pure state on the keying layer.
- Other fixing processes have been described wherein various chemical keying adjuvants are added to a dispersion of the fluorocarbon resin. Such processes are disclosed more particularly in French Patents 1,020,903, 1,536,986, 1,537,129, 1,386,898, 2,024,171.
- The coatings prepared by these various processes have the following disadvantage in common: their resistance to abrasion is just sufficient to satisfy the conditions of use associated with cooking utensils.
- To obviate these disadvantages, it has been proposed to make composite coatings wherein an added porous layer or "hard base" is deposited on the utensil metal before being covered with the fluorocarbon resin. In practice, these hard bases are obtained by depositing metals, alloys or oxides of these metals on the metal surface, e.g. aluminium, or alternatively cermets. Such intermediate layers are deposited in practice by spraying the said substances by means of a plasma or flame gun.
- These various processes are very expensive. Also, keying the fluorocarbon resin on the hard layer is not always easy, and it is also often difficult to produce a coating having the suitable degree of porosity together with suitable hardness.
- Another process is described in French Patent 1,536,889 wherein a single layer of vitreous balls of a diameter of about 10 to 500 microns is deposited on the metal surface to give approximately 15 balls per square centimetre. These balls are fixed by a binder which covers them and the binder is in turn covered by an aqueous dispersion of particles of the fluorocarbon resin.
- The process, however, is complicated to perform, because it is difficult to ensure regular distribution of the balls on the metal surface. Also, the process is complex. In some countries, including France, the use of chromic acid and chromates for the production of kitchen articles is prohibited because of the risks of these products to public health.
- The object of this invention is to obviate the disadvantages of the various processes set out above. It has as its object more particularly to produce cheap kitchen utensils having abrasion-resistance equal to those comprising a suitable hard base and without the use of any toxic or prohibited product.
- The present invention is based on the following unexpected finding. If, instead of producing a hard intermediate layer, a mixture of unsintered fluorocarbon resin particles and sintered glaze particles is hardened, the resulting coating has outstanding abrasion-resistance and requires no chromic acid for its fixing on the metal base.
- According to the invention, a non-stick coating composition, for example for the coating of metal surfaces such as aluminium discs adapted to form cooking utensils, comprises an aqueous dispersion of unsintered fluorocarbon resin particles and sintered glaze particles having a melting point above 400°C,

the proportion of said resin being at least 100% by dry weight of that of the dry weight of said glaze.

Experiment has given the surprising result that the said association of unsintered fluorocarbon resin and sintered substance gives an intrinsically hard fluorocarbon coating having excellent abrasion-resistance while retaining sufficient non-stick quality in operation.

Preferably, the sintered glaze used has a melting temperature of between 500 and 600°C.

The sintered substance must, *inter alia*, be free from lead and more generally any metal whose melting point is below 400°C, for reasons which will be explained hereinafter.

According to one advantageous embodiment, the composition of the non-stick coating is characterised in that the percentages of the fluorocarbon resin and of the sintered glaze may vary as follows:

A. In the case of the fluorocarbon resin between 50 and 30% by weight of the total composition (including water);

B. In the case of the sintered glaze between 10 and 30% by weight of the total composition.

From the above-indicated numerical data, a specific non-stick coating composition can be obtained from an aqueous suspension containing a total of 60% of anhydrous products and 40% water.

According to another important feature of the invention, the sintered glaze is advantageously formed from angular particles whereby the fluorocarbon resin can be keyed on said particles so that the latter cannot be shifted under the effect of the pressure exerted, for example, by a spatula, since that would destroy the cohesion of the coating. An effect of this kind is found in the case of the use of balls according to the prior-art process indicated hereinbefore.

To reinforce this cohesion, the sintered glaze is preferably selected—according to another feature of this invention—so that the grains of the glaze have a grain size of the order of that of the particles of fluorocarbon resin and between 3 and 20 microns, their average size being 8 microns.

A preferred but non-limitative embodiment of this invention comprises selecting a total coating thickness of between 30 and 60 microns, preferably between 30 and 35 microns, to allow a statistical distribution of the grains of sintered glaze comprising, in the direction of the thickness, on average three sintered glaze particles completely enclosed in fluorocarbon resin. A thickness of this kind also provides better cooking heat transmission through the coating.

Experiment has shown that the maximum thickness of the total coating which can be expected without the danger of cracking of

the coating after sintering of the polymerised fluorocarbon is 60 microns. If it is required to produce coatings of a thickness of above 60 microns, a number of successive applications are required, the products being placed in the kiln between the first and second applications, and so on between two subsequent successive applications, each passage through the kiln ensuring sintering of the last-deposited layer. However, excessive thickness has an adverse effect on the proper transmission of the heat through the non-stick coating to the food being cooked.

According to another feature of the invention, grinding and hardening adjuvants, such as potassium and sodium silicate, caustic potash, and boric acid, are added to a sintered glaze aqueous suspension to be used to form a composition of the invention, which suspension is known in the French glaze industry as a sintered glaze slip.

These adjuvants act as suspension agents for the ground sintered substance, the viscosity of which can thus be adjusted before being placed in the kiln. More particularly, boric acid and potash serve to facilitate the wetting of aluminium by the slip and adjust the pH of the latter to a value of between 10 and 11 in the case of the slips used for coating aluminium. The pH is thus very close to that of the aqueous polytetrafluoroethylene (PTFE) dispersion intended for mixing with the slip, and which has a value of between 9.5 and 11. This allows very easy mixing of the slip and of the PTFE dispersion.

The preferred fluorocarbon resin most usually employed within the scope of the invention is polytetrafluoroethylene, but it may be also selected from the fluorine copolymers such as tetrafluoroethylene-hexafluoropropylene copolymer and polyethylene-tetrafluoroethylene.

The coating provided by the invention may also be coloured by pigments, either by grinding the pigments with the slip to give the particles of the latter the required fineness, or by incorporating them in the mixture formed from the slip and the fluorocarbon resin, or by mixing the pigments with the dispersion of fluorocarbon resin.

For industrial application, the non-stick coating composition to which the invention relates is spread on the entire surface for coating of metal sheets, discs or plates, at least over one of the surfaces thereof, so as to form a continuous coating, the thickness of which is preferably between 30 and 60 microns as indicated hereinbefore. The coating may be spread by any suitable means, for example a brush, sponge, or a pneumatic spray gun (of the Airless type).

The composition is then subjected to drying at 70—90°C by hot air or by infra-red

radiation, or by any other means compatible with maintaining good cohesion between its constituent elements. The drying time is calculated so as to ensure complete evaporation of the water contained in the aqueous suspension. At the end of this drying operation the composition is then sintered in the kiln at a temperature of about 400°C for a period of from 10 to 15 minutes.

It will be apparent that in view of the specific characteristics of the angular shape and grain size in accordance with which the sintered glaze particles are selected, the sintered glaze must be free from lead and more generally from any metals with a melting point below 400°C, in order to prevent such metals from melting during sintering in the kiln at the exact temperature of 400°C, and entraining with them the sintered glaze particles by gravity towards the bottom points of the coating composition, since this would destroy the regular statistical distribution of

the particles in stratified layers within the polymerised fluorocarbon.

The coating provided by the invention has outstanding hardness, compactness and abrasion-resistance, while having a non-stick surface for food, thus preventing them from sticking to the kitchen utensil and offering advantages comparable with those of pure PTFE coatings.

By using the above-described production process it is possible to produce any manufactured articles, more particularly cooking utensils, formed by known drawing or pressing operations or by any other means from sheets, discs or plates coated with the composition in question. The resulting manufactured articles are distinguished in that they comprise a non-stick but intrinsically hard polymerised fluorocarbon coating.

Three advantageous examples of preparing a sintered glaze slip will now be given without limiting force.

EXAMPLE 1.

A slip was prepared having the following composition:

	Bayer-Rickann AL 6110 (sintered glaze particles free of lead)	1000 g	
	Sodium silicate d.1.33 liquid	1 part	} 10 g
	Potassium silicate d.1.33 liquid	3 parts	
	Caustic potash	10 g	
	Boric acid	40 g	
	Water	350 g	

The mixture is ground, for example, in a high-density porcelain ball mill to a fineness of 0.1 on a Bayer 16 900 mesh per square cm frusto-conical screen (DIN 1171-E 130).

When this fineness has been obtained, the slip is mixed with the aqueous PTFE dispersion in the following proportion:

Aqueous PTFE dispersion containing 60% solids	1000 g
Slip	150 g

This composition is applied by spray gun or any other means to an aluminium disc which has previously been roughened by sand-blasting or, preferably, by chemical attack with hydrochloric acid. It is then dried at about 80–90°C to evaporate the liquid phase, and then sintered in a kiln at 400°C.

EXAMPLE 2.

Slip from sintered product AL 8 made by Messrs. Ferro.

Ferro AL 8 (sintered glaze particles)	1000 g
Add Ferro AL 30 (liquid grinding and hardening adjuvant)	120 g
Water	300 g

Grinding and the sequence of operations

are identical to the description in Example 1.

Other sintered products, for example sintered glaze particles available under the Trade Names Ferro CN500 or Bayer 6100, may be used to prepare the slip which can be used to produce the desired composition.

The percentage of slip used in the coating composition may vary between 5 and 50% by weight depending upon the degree of hardness or the final non-stick property required of the coating.

The coating may be coloured by pigments as indicated hereinbefore.

With regard to the sintered products, good results are obtained with compositions satisfying, for example, the following formulae:

SiO ₂	30–45%
B ₂ O ₃	0–10%
LiO ₂ + Na ₂ O + K ₂ O	25–35%
TiO ₂	15–30%
Al ₂ O ₃	0–10%

Other oxides may also be incorporated in the composition in a proportion of from 0 to 10%, i.e.:



More particularly, experiment has shown that

one of the five sintered glaze formulae indicated in the following Table is also suitable for the production of a coating composition according to the invention.

Formulae		No. 1	No. 2	No. 3	No. 4	No. 5
5	Na ₂ O	% 22.2	% 16.8	% 17.8	% 24.8	% 20.3
	K ₂ O	7.2	3.7	3.9	3.7	5.0
	Li ₂ O	—	—	—	—	3.0
	SiO ₂	32.1	21.0	22.3	21.5	21.9
	Al ₂ O ₃	7.7	5.9	—	1.0	5.4
10	B ₂ O ₃	19.9	33.66	35.6	19.6	24.0
	Sb ₂ O ₃	5.8	4.8	5.1	4.9	5
	NaF	2.3	8.0	8.6	11.0	—
	AlF ₃	1.6	5.4	5.7	7.0	—
	CaF ₂	1.2	0.8	1.0	1.5	1
15	ZnO	—	—	—	4.0	6
	LiF	—	—	—	—	8.4

In Examples 1 and 2, the sodium and potassium silicates or the liquid adjuvant Ferro AL 30 act as grinding adjuvants for the sintered glaze. They may also be replaced by metasilicates of the same metals. In either case, they form suspension agents for the ground sintered glaze and contribute to adjustment of the viscosity of the mixture and to the hardening of the enamel coating before being placed in the kiln.

As indicated, the present invention relates not only to the non-stick coating composition and its application to a non-stick coating production process, but also the manufactured articles obtained by using this production process or by means of this composition.

WHAT WE CLAIM IS:—

1. A non-stick coating composition comprising an aqueous dispersion of unsintered fluorocarbon resin particles and sintered glaze particles having a melting point above 400°C, the proportion of said resin being at least 100% by dry weight of that of the dry weight of said glaze.

2. A composition as claimed in Claim 1, wherein the percentage content of fluorocarbon resin and sintered glaze particles are substantially as follows:

A. in the case of the fluorocarbon resin, between 50% and 30% by weight of the total composition;

B. in the case of the sintered glaze particles, between 10 and 30% by weight of the total composition.

3. A composition as claimed in Claim 1 or Claim 2 wherein the sintered glaze particles are angular.

4. A composition as claimed in any one of the preceding claims wherein the sintered glaze has a melting point between 500 and 600°C.

5. A composition as claimed in any one of the preceding claims wherein the grains of

the sintered glaze slip have a grain size of between 3 and 20 microns, their average size being 8 microns.

6. A composition as claimed in any one of the preceding claims wherein the sintered glaze particles have been introduced into an aqueous dispersion of the fluorocarbon resin as an aqueous suspension containing also grinding and hardening adjuvants.

7. A composition as claimed in Claim 6 wherein said suspension of sintered glaze particles contains sodium and potassium silicates, caustic potash and boric acid as grinding and hardening adjuvants.

8. A composition as claimed in any one of the preceding claims wherein the fluorocarbon resin is polytetrafluoroethylene.

9. A composition according to any one of Claims 1 to 7, wherein the fluorocarbon resin is tetra-fluoroethylene-hexafluoro-propylene copolymer or polyethylene-tetrafluoroethylene.

10. A composition as claimed in any one of the preceding claims having a pH substantially between 10 and 11.

11. A composition as claimed in any one of the preceding claims wherein the sintered glaze particles are free from lead.

12. A composition as claimed in any one of the preceding claims wherein the sintered glaze particles are formed from a mixture of oxides.

13. A composition as claimed in Claim 12 wherein the mixture of oxides satisfies the formula:

	by weight	
SiO ₂	30—45%	95
B ₂ O ₃	0—10%	
Li ₂ O + Na ₂ O + K ₂ O	25—35%	
TiO ₂	15—30%	
Al ₂ O ₃	0—10%	100
ZrO ₂	0—10%	
SnO ₂	0—10%	
ZnO	0—10%	
CaO	0—10%	
P ₂ O ₅	0—10%	105

one of the five sintered glaze formulae indicated in the following Table is also suitable for the production of a coating composition according to the invention.

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		%	%	%	%	%
5	Na ₂ O	22.2	16.8	17.8	24.8	20.3
	K ₂ O	7.2	3.7	3.9	3.7	5.0
	Li ₂ O	—	—	—	—	3.0
	SiO ₂	32.1	21.0	22.3	21.5	21.9
	Al ₂ O ₃	7.7	5.9	—	1.0	5.4
10	B ₂ O ₃	19.9	33.66	35.6	19.6	24.0
	Sb ₂ O ₃	5.8	4.8	5.1	4.9	5
	NaF	2.3	8.0	8.6	11.0	—
	AlF ₃	1.6	5.4	5.7	7.0	—
	CaF ₂	1.2	0.8	1.0	1.5	1
15	ZnO	—	—	—	4.0	6
	LiF	—	—	—	—	8.4

In Examples 1 and 2, the sodium and potassium silicates or the liquid adjuvant Ferro AL 30 act as grinding adjuvants for the sintered glaze. They may also be replaced by metasilicates of the same metals. In either case, they form suspension agents for the ground sintered glaze and contribute to adjustment of the viscosity of the mixture and to the hardening of the enamel coating before being placed in the kiln.

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B. in the case of the sintered glaze particles, between 10 and 30% by weight of the total composition.

3. A composition as claimed in Claim 1 or Claim 2 wherein the sintered glaze particles are angular.

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5. A composition as claimed in any one of the preceding claims wherein the grains of

the sintered glaze slip have a grain size of between 3 and 20 microns, their average size being 8 microns.

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7. A composition as claimed in Claim 6 wherein said suspension of sintered glaze particles contains sodium and potassium silicates, caustic potash and boric acid as grinding and hardening adjuvants.

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LiO ₂ + Na ₂ O + K ₂ O	25—35%	
TiO ₂	15—30%	
Al ₂ O ₃	0—10%	100
ZrO ₂	0—10%	
SnO ₂	0—10%	
ZnO	0—10%	
CaO	0—10%	
P ₂ O ₅	0—10%	105



14. A composition as claimed in any one of the preceding claims which contains pigments.
15. A composition as claimed in Claim 1 and substantially as described in the Examples.
- 5 16. A process for the production of a non-stick coating on a metal surface by the application of a composition as claimed in any one of the preceding claims wherein said composition is applied to said metal surface, the resulting coating is dried to evaporate the water therefrom, and then the polymerised fluorocarbon is sintered by passing it through a kiln.
- 10 17. A process as claimed in Claim 16 wherein the metal is aluminium.
- 15 18. A process as claimed in Claim 17 wherein the metal surface is a surface of a disc.
19. A process as claimed in any one of Claims 16, 17 and 18 wherein the thickness of the coating on the metal surface before drying is between 30 and 60 microns.
- 20 20. A process as claimed in Claim 19 wherein said thickness is between 30 and 35 microns.
21. A process as claimed in Claim 16 and substantially as described herein.
22. A manufactured article having at least one surface thereof coated by a process as claimed in any one of Claims 16 to 21 with an intrinsically hard fluorocarbon resin non-stick coating.
23. An article as claimed in Claim 22 which is a cooking utensil.
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For the Applicants,
F. J. CLEVELAND & COMPANY,
Chartered Patent Agents,
Lincolns Inn Chambers,
40/43 Chancery Lane,
London WC2A 1JQ.

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