

## Description

BACKGROUND OF THE INVENTION

5 This invention relates to coatings systems, such as for cookware, which minimize sticking. More particularly, it relates to multilayer coating systems that can be used on smooth, untreated substrates.

Generally in the art a metal or glass substrate is roughened by some means before the first layer of coating is applied so that mechanical bonding will assist chemical adhesive means in holding the coating onto the substrate. Typical roughening means include acid etching, sand-blasting, grit-blasting, and baking a rough layer  
10 of glass, ceramic or enamel frit onto the substrate. The problem of adhesion of non-stick coatings to substrates is exacerbated by the nature of the coatings. If the coating is optimized for release to prevent food particles from sticking to it, easy clean-up after cooking, durability or to facilitate low friction sliding contact, almost by definition there will be difficulties in making it adhere well to the substrate.

The substrate can be metal, often aluminum or stainless steel used for cookware or industrial applications. It can be glass or ceramic. It might even be plastic for microwave oven cookware, or it could be an industrial article such as a saw made of carbon steel. Whatever the substrate or the application, if it is necessary to roughen the substrate to make the coating adhere, that at least adds cost and can cause other difficulties including creating a rough profile which can protrude or telegraph through the coating. This is especially undesirable when smoothness is sought, such as for saws and steam irons. The environmental cost of disposing of etchant materials can be significant. Sometimes, especially for glass and ceramic substrates, it also can cause unacceptable weakness or brittleness of the substrate.  
20

Means of enhancing adhesion of non-stick coatings to a substrate are illustrated by the following patents.

U.S. 2,562,118-Osdal (1951) uses a mixture of phosphoric and chromic acids in a coating containing polytetrafluoroethylene (PTFE) for use directly on metal or glass. This can cause some inherent etching of the substrate. Better adhesion would be desirable.  
25

U.S. 4,049,863 - Vassiliou (1977) teaches a primer containing fluoropolymer, such as PTFE, colloidal silica and a polyamide imide (PAI), along with other constituents, applied by various techniques to a substrate that is preferably pretreated by grit blasting, flame spraying of metals or metal oxides or frit coating, or to phosphated and chromated metals. The PTFE:PAI ratio can be 1:9. The primer coat is ordinarily applied to a dry film thickness (DFT) of about 2-15 microns ( $\mu\text{m}$ ). After air drying, the primer is topcoated with a conventional fluoropolymer enamel and baked. (Parts, percentages and proportions herein are by weight except where indicated otherwise.)  
30

Although U.S. 4,259,375 - Vassiliou (1981) teaches applying a decorative fluoropolymer coating on a primer which is applied directly to the substrate, the implication is that the usual roughened substrate is used.

U.S. 3,801,379 - Blackwell (1974) applies a poly(arylene sulfide) coating such as polyphenylene sulfide (PPS) directly to an aluminum substrate after treating the substrate with hot water or steam. Preferably the coating is done with the substrate at 455°C, causing flocking of the coating. The thickness of the coating is not disclosed, and the PPS can contain 5-20% PTFE.  
35

Canadian 887,122 - Fang (1971) provides a single coating of PAI and PTFE on a metal substrate with a concentration gradient from mostly PAI at the substrate to mostly PTFE at the air interface. This is applied as a single coat without any special primer on ordinary steel or sand-blasted aluminum.  
40

British 1,512,495 (SEB) (1978) applies a PAI coating containing PTFE powder at a DFT of 5-100 microns to a metal or glass substrate that has been merely de-greased and not roughened. The minimum ratio of PTFE:PAI is 1:7. This then is the undercoat on which a PTFE powder topcoat is applied. However, the PTFE in the undercoat at these thicknesses can lead to failure of intercoat adhesion.  
45

European application 100,889 - Gebauer (1984) describes thicker coatings containing certain perfluorocarbon resins, PPS, lithium hydroxide, and silica and asserts they are superior to prior art primer coatings on the order of 10 microns thickness. If the substrate is smooth, he teaches that it can be roughened by sand blasting or etching.

U.S. 4,177,320 and 4,139,576 - both Yoshimura, et al, (1979) teach an undercoat of PPS or PPS plus PAI or polyimide with surface active agents on sand-blasted rough aluminum at a DFT of 15 or 20-25 microns. As in many of these patents, the need for roughening the substrate to obtain adequate adhesion and durability adds considerable costs.  
50

Coatings systems including primers, intermediate and top coats useful with the present invention are described in various patents including:  
55

U.S. 4,049,863 - Vassiliou (1977);

U.S. 4,118,537 - Vary and Vassiliou (1978);

U.S. 4,123,401 - Berghmans and Vary (1978);

U.S. 4,252,859 - Concannon and Vary (1981);

U.S. 4,351,882 - Concannon (1982); all incorporated herein by reference.

## 5 SUMMARY OF THE INVENTION

The present invention, in certain of its embodiments, provides a coating system comprising a substrate, preferably of glass or ceramic, with a multi-layer non-stick coating, comprising two undercoats, a primer, a topcoat and up to one or more intermediate coats, wherein:

- 10 the substrate is free of contaminants that would prevent adhesion of the undercoat,
- the first undercoat is applied to the substrate and consists essentially of polysiloxane resin and has a thickness in the range of 0.1-5.0 microns,
- the second undercoat is applied to the first undercoat and consists essentially (on a weight basis after air drying but before baking) up to 8%, preferably 3-8%, surfactant, up to 20%, preferably 10-20%, fine-particle
- 15 silica, the balance polyamide imide, and has a dry film thickness in the range of 0.1-5.0 microns,
- the primer is applied to the second undercoat and comprises perfluorocarbon resin and at least one of polyamide imide, polyarylene sulfide and polyether sulfone and has a dry film thickness in the range of 2-15 microns, and
- the topcoat comprises perfluorocarbon resin.

20

## DETAILED DESCRIPTION

The present invention permits not only lower cost by avoiding the roughening of the substrate but also smoother coated surfaces which can be advantageous for release on cookware.

- 25 When coating systems otherwise according to the invention are attempted on smooth substrates without the required thin undercoat, the film can be removed too easily by ordinary crosshatch or finger-nail scratch tests. Also, when the undercoat is thicker than stated above, it tends to crack the midcoat and cause rippling of the topcoat. With use of the undercoat on smooth substrates, treated only by washing to remove grease and any other contaminants which might interfere with adhesion, coating systems of the invention give good
- 30 food release and good resistance to usual durability tests such as the "tiger paw" cooking tests involving a weighted holder with multiple ball point pen shafts rotating around the inside of a frying pan during cooking tests. Satisfactory results are not obtained without the undercoat or with PTFE in the undercoat or with too thick an undercoat.

- Typical prior art preparation of surfaces to enhance adhesion of a release coating has involved etching or sand or grit blasting to develop a surface profile. The profile measured in average microinches using a model
- 35 RT 60 surface roughness tester made by Alpa Co. of Milan, Italy. The present invention is particularly useful with substrates having a profile of less than 2.5, preferably less than 1.3 microns (100, preferably less than 50 micro inches).

- In the following examples, the polysiloxane resin is that of U.S. Patents 4,369,279 - Emerich (1983),
- 40 4,252,702 - Wald (1987), and 4,183,998 - Vassiliou (1980); the polyamide imide, colloidal silica and dispersions preferably are those of U.S. Patent 4,049,863 - Vassiliou (1977); the PTFE blends are those of U.S. Patents 4,252,859 and 4,351,883 - Concannon (1982); the ultramarine blue is that of U.S. Patent 4,425,448 - Concannon and Rummel (1984); the polyether sulfone is that of U.S. Patent 3,981,945 (1976), 4,090,993 (1978) - both
- 45 Atwood et al, and 4,131,711 (1978) - Atwood, and the polyarylene sulfide is the polyphenylene sulfide of U.S. Patent 4,287,112 (1981) - Berghmans.

## EXAMPLE

- A piece of "Pyrex" borosilicate glass made by Corning Glass is washed to remove contaminants. It is then
- 50 coated with a thin layer of polysiloxane resin formulation to a DFT of 0.5-5.0, preferably 0.25-2.5, more preferably 1.25 microns and air dried. The formulation is:

55

FIRST UNDERCOAT

| <u>Ingredient</u>       | <u>% by weight</u> |
|-------------------------|--------------------|
| polysiloxane resin      | 21.0               |
| 6-2230 from Dow Corning |                    |
| petroleum xylol         | 39.5               |
| toluene                 | 39.5               |
| <b>TOTAL</b>            | <b>100.00</b>      |

This produces a first undercoat on which is then applied a second undercoat as follows.

The second undercoat comprising polyamide imide, colloidal silica and surfactant is sprayed on the first undercoat to a DFT of 0.1-5.0, preferably 0.25-2.5, more preferably 1.25 microns. This undercoat is permitted to air dry, then a primer coat of polyamide imide, PTFE, colloidal silica, TiO<sub>2</sub>-coated mica, pigmentation such as ultramarine blue, TiO<sub>2</sub> and other pigments, is sprayed onto the undercoat, to a DFT of 5.0 to 7.5 microns, and a topcoat is sprayed to a DFT of 15 to 17.5 microns (wet-on-wet) on the primer coat, containing PTFE, decomposable acrylic resin to aid in coalescence, and TiO<sub>2</sub> coated mica. The coating system is then baked at 149°C for 10 minutes followed by 427°C for 5 minutes. The substrate should be above 416°C at least 3 minutes in a commercial operation where the thermal inertia of the substrate can cause slow heating. As is shown in the art, DFT can be controlled by the time of spraying or by dilution, and other application techniques such as roller coating can be used.

The thicknesses of the undercoats and the primer coat are both important to avoid loss of intercoat adhesion. The topcoat thickness is preferred but can be varied. Thicker topcoats under some circumstances can give improved performance. The primer coat weight ration of PTFE to PAI preferably is in the range of 2:1 to 7:1 with about 4:1 most preferred.

The following tables show the formulations for these layers.

SECOND UNDERCOAT

| <u>Ingredient</u>                | <u>% by weight</u> | <u>(dry basis and range)</u> |
|----------------------------------|--------------------|------------------------------|
| furfuryl alcohol                 | 2.4                | --                           |
| polyamide imide solution         | 26.02              | 78.74                        |
| AI-10 from Amoco                 |                    | (balance)                    |
| deionized water                  | 66.48              | --                           |
| colloidal silica                 | 4.60               | 15.86                        |
| Ludox AM from Du Pont            |                    | (10-20)                      |
| surfactant                       | 0.5                | 5.4                          |
| Triton X100 from Rohm & Haas Co. |                    | (3-8)                        |
| <b>TOTAL</b>                     | <b>100.00</b>      | <b>100.00</b>                |

**PRIMER**

| <u>Ingredient</u>                   | <u>% by weight (wet basis)</u> |
|-------------------------------------|--------------------------------|
| furfuryl alcohol                    | 1.85                           |
| polyamide imide solution            | 18.09                          |
| deionized water                     | 52.01                          |
| TiO <sub>2</sub> -coated mica flake | 0.06                           |
| "Afflair" from Merck                |                                |
| PTFE dispersion                     | 20.95                          |
| T-30 from Du Pont                   |                                |
| colloidal silica                    | 3.62                           |
| ultramarine blue pigment            | 3.15                           |
| 53% solids dispersed in water       |                                |
| red vion oxide pigment              | 0.27                           |
| 45% solids dispersed in water       |                                |
| <b>TOTAL</b>                        | <b>100.00</b>                  |

**TOPCOAT**

The preferred topcoat is that of example 1 of U.S. Patent 4,118,537.

When the polysiloxane undercoat is used, no loss of adhesion is found after 8 hours immersion in boiling water. In comparison, the coating on Pyrex glass starting with the second undercoat (PAI) without the polysiloxane first undercoat completely delaminated from the substrate after 5 minutes in boiling water.

Alternatively, the coats above the undercoat and primer (topcoat and optional intermediate coats) can be those of U.S. Patents 4,810,609; 4,252,859; 4,351,882, and 4,425,448, and combinations thereof. Also the thin undercoats of the invention can also be used on substrates roughened in various ways known in the art to make coating systems even better than without such undercoats.

**Claims**

1. A coated substrate comprising a substrate with a multi-layer non-stick coating, comprising two undercoats, a primer, a topcoat and up to one or more intermediate coats, wherein:
  - the substrate is free of contaminants that would prevent adhesion of the undercoat,
  - the first undercoat is applied to the substrate and consists essentially of polysiloxane resin and has a thickness in the range of 0.1-5.0 microns,
  - the second undercoat is applied to the first undercoat and consists essentially (on a weight basis after air drying but before baking) up to 8% surfactant, up to 20% fine-particle silica, the balance polyamide imide, and has a dry film thickness in the range of 0.1-5.0 microns,
  - the primer is applied to the second undercoat and comprises perfluorocarbon resin and at least one of polyamide imide, polyarylene sulfide and polyether sulfone and has a dry film thickness in the range of 2-15 microns, and
  - the topcoat comprises perfluorocarbon resin.
2. The coated substrate of Claim 1 wherein the coating comprises at least one intermediate coat containing the ingredients of the primer.
3. The coated substrate of Claim 1 wherein the substrate is glass or ceramic.
4. The coated substrate of Claim 3 wherein the substrate before coating has a surface roughness profile less than 2.5 microns (100 micro inches).
5. The coated substrate of Claim 3 wherein the substrate before coating has a surface roughness profile less than 1.3 microns (50 micro inches).

**PRIMER**

| <u>Ingredient</u>                   | <u>% by weight (wet basis)</u> |
|-------------------------------------|--------------------------------|
| furfuryl alcohol                    | 1.85                           |
| polyamide imide solution            | 18.09                          |
| deionized water                     | 52.01                          |
| TiO <sub>2</sub> -coated mica flake | 0.06                           |
| "Afflair" from Merck                |                                |
| PTFE dispersion                     | 20.95                          |
| T-30 from Du Pont                   |                                |
| colloidal silica                    | 3.62                           |
| ultramarine blue pigment            | 3.15                           |
| 53% solids dispersed in water       |                                |
| red vion oxide pigment              | 0.27                           |
| 45% solids dispersed in water       |                                |
| <b>TOTAL</b>                        | <b>100.00</b>                  |

**TOPCOAT**

The preferred topcoat is that of example 1 of U.S. Patent 4,118,537.

When the polysiloxane undercoat is used, no loss of adhesion is found after 8 hours immersion in boiling water. In comparison, the coating on Pyrex glass starting with the second undercoat (PAI) without the polysiloxane first undercoat completely delaminated from the substrate after 5 minutes in boiling water.

Alternatively, the coats above the undercoat and primer (topcoat and optional intermediate coats) can be those of U.S. Patents 4,810,609; 4,252,859; 4,351,882, and 4,425,448, and combinations thereof. Also the thin undercoats of the invention can also be used on substrates roughened in various ways known in the art to make coating systems even better than without such undercoats.

**Claims**

1. A coated substrate comprising a substrate with a multi-layer non-stick coating, comprising two undercoats, a primer, a topcoat and up to one or more intermediate coats, wherein:
  - the substrate is free of contaminants that would prevent adhesion of the undercoat,
  - the first undercoat is applied to the substrate and consists essentially of polysiloxane resin and has a thickness in the range of 0.1-5.0 microns,
  - the second undercoat is applied to the first undercoat and consists essentially (on a weight basis after air drying but before baking) up to 8% surfactant, up to 20% fine-particle silica, the balance polyamide imide, and has a dry film thickness in the range of 0.1-5.0 microns,
  - the primer is applied to the second undercoat and comprises perfluorocarbon resin and at least one of polyamide imide, polyarylene sulfide and polyether sulfone and has a dry film thickness in the range of 2-15 microns, and
  - the topcoat comprises perfluorocarbon resin.
2. The coated substrate of Claim 1 wherein the coating comprises at least one intermediate coat containing the ingredients of the primer.
3. The coated substrate of Claim 1 wherein the substrate is glass or ceramic.
4. The coated substrate of Claim 3 wherein the substrate before coating has a surface roughness profile less than 2.5 microns (100 micro inches).
5. The coated substrate of Claim 3 wherein the substrate before coating has a surface roughness profile less than 1.3 microns (50 micro inches).



6. The coated substrate of Claim 1 wherein the second undercoat contains 10-20% fine-particle silica and 3-8% surfactant.
- 5 7. The coated substrate of Claim 6 wherein the undercoat has a dry film thickness of 0.25-2.5 microns.
8. The coated substrate of Claim 7 wherein the primer has a dry film thickness of 5.0-7.5 microns.
9. The coated substrate of Claim 1 wherein, before application of the undercoat, the surface of the substrate has been treated to remove contaminants that would interfere with adhesion but has not been etched or mechanically roughened.

#### Patentansprüche

- 15 1. Überzogenes Substrat, umfassend ein Substrat mit einem nichtklebenden Mehrschichtenüberzug, umfassend zwei Grundschichten, einen Primer, eine Deckschicht und bis zu einer oder mehrere Zwischenschichten, worin:  
das Substrat frei von Verunreinigungen ist, die eine Haftung der Grundschicht verhindern würden,  
20 die erste Grundschicht auf das Substrat aufgetragen wird und im wesentlichen aus Polysiloxan-Harz besteht und eine Dicke im Bereich von 0,1-5,0 µm aufweist,  
die zweite Grundschicht auf die erste Grundschicht aufgetragen wird und im wesentlichen besteht aus (bezogen auf das Gewicht nach dem Lufttrocknen, jedoch vor dem Trocknen in einem Ofen) bis zu 8 % eines oberflächenaktiven Mittels, bis zu 20 % Feinteilchen-Kieselsäure, der Rest Polyamidimid, und eine trockene Filmdicke im Bereich von 0,1-5,0 µm besitzt, der Primer auf die zweite Grundschicht aufgetragen wird und Perfluorkohlenstoff-Harz und wenigstens eines von Polyamidimid, Polyarylsulfid und Polyethersulfon umfaßt und eine trockene Filmdicke im Bereich von 2-15 µm aufweist, und die Deckschicht Perfluorkohlenstoff-Harz umfaßt.
- 30 2. Überzogenes Substrat nach Anspruch 1, worin der Überzug wenigstens eine Zwischenschicht umfaßt, die die Bestandteile des Primers enthält.
3. Überzogenes Substrat nach Anspruch 1, worin das Substrat Glas oder Keramik ist.
- 35 4. Überzogenes Substrat nach Anspruch 3, worin das Substrat vor dem Überziehen ein Oberflächenrauheitsprofil von weniger als 2,5 µm (100 µin.) aufweist.
5. Überzogenes Substrat nach Anspruch 3, worin das Substrat vor dem Überziehen ein Oberflächenrauheitsprofil von weniger als 1,3 µm (50 µin.) aufweist.
- 40 6. Überzogenes Substrat nach Anspruch 1, worin die zweite Grundschicht 10-20 % Feinteilchen-Kieselsäure und 3-8 % oberflächenaktives Mittel enthält.
7. Überzogenes Substrat nach Anspruch 6, worin die Grundschicht eine trockene Filmdicke von 0,25-2,5 µm aufweist.
- 45 8. Überzogenes Substrat nach Anspruch 7, worin der Primer eine trockene Filmdicke von 5,0-7,5 µm aufweist.
9. Überzogenes Substrat nach Anspruch 1, worin vor dem Auftragen der Grundschicht die Oberfläche des Substrats zur Entfernung von Verunreinigungen, die die Haftung stören würden, behandelt, jedoch nicht angeätzt oder mechanisch aufgerauht worden ist.

#### Revendications

- 55 1. Substrat revêtu, comprenant un substrat avec un revêtement non collant, multicouche, comprenant deux sous-couches, une couche primaire, une couche supérieure et jusqu'à une ou plusieurs couche(s) intermédiaire(s), dans lequel :  
le substrat est exempt d'impuretés qui empêcheraient l'adhésion de la sous-couche,



la première sous-couche est appliquée sur le substrat et est essentiellement constituée de résine de polysiloxane et a une épaisseur dans la gamme de 0,1 à 5,0 micromètres,

5 la seconde sous-couche est appliquée sur la première sous-couche et est essentiellement constituée (sur une base pondérale après séchage à l'air, mais avant la cuisson) de jusqu'à 8 % d'agent tensioactif, jusqu'à 20 % de silice en particules fines, et de polyamide imide pour le reste, et a une épaisseur de pellicule sèche dans la gamme de 0,1 à 5,0 micromètres,

10 la couche primaire est appliquée sur la seconde sous-couche et comprend une résine perfluorocarbonée et au moins un constituant choisi parmi un polyamide imide, un sulfure de polyarylene et une polyéthersulfone, et a une épaisseur de pellicule sèche dans la gamme de 2 à 15 micromètres, et

la couche supérieure comprend une résine perfluorocarbonée.

2. Substrat revêtu selon la revendication 1, dans lequel le revêtement comprend au moins une couche intermédiaire contenant les ingrédients de la couche primaire.
- 15 3. Substrat revêtu selon la revendication 1, dans lequel le substrat est du verre ou de la céramique.
4. Substrat revêtu selon la revendication 3, dans lequel le substrat, avant d'être revêtu, a un profil de rugosité de surface inférieur à 2,5 micromètres.
- 20 5. Substrat revêtu selon la revendication 3, dans lequel le substrat, avant d'être revêtu, a un profil de rugosité de surface inférieur à 1,3 micromètre.
6. Substrat revêtu selon la revendication 1, dans lequel la seconde sous-couche contient 10 à 20 % de silice en particules fines et 3 à 8 % d'agent tensioactif.
- 25 7. Substrat revêtu selon la revendication 6, dans lequel la sous-couche a une épaisseur de pellicule sèche de 0,25 à 2,5 micromètres.
8. Substrat revêtu selon la revendication 7, dans lequel la couche primaire a une épaisseur de pellicule sèche de 5,0 à 7,5 micromètres.
- 30 9. Substrat revêtu selon la revendication 1, dans lequel, avant l'application de la sous-couche, la surface du substrat a été traitée pour éliminer des impuretés qui interféreraient avec l'adhésion, mais elle n'a pas été chimiquement attaquée ni mécaniquement rendue rugueuse.