GLASSY SURFACE FUNCTIONALISATION BY NANO–MODIFIED "SOL–GEL" TECHNOLOGY

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Glassy surface functionalisation by nano-modified "Sol-Gel" technology

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1. Introduction

Glassy surfaces, especially enamels, ceramic glazes and glass, not always present the desired surface properties in order to achieve new performances. The realised investigations clearly show that those properties are not achievable by modifying the composition of those surfaces. That is why it is often necessary to treat them superficially, so that they can obtain the missing property (ies). The superficial treatment in question can be realised by **CVD** (Chemical Vapour Deposition"), **PVD** (Physical Vapour Deposition), **FS** (Flame-Spray), or by **Chemical Nano-technology** (= **Sol-Gel-technology**). Below you will find a detailed explanation about this last process, about the multiple functions that can be obtained and more particularly about **"NanoClean", a nano-modified "sol-gel" layer**, transforming an enamelled surface into a surface presenting anti-adherent properties.

2. A few examples of achievable additional surface properties through "sol-gel"-technology

The "sol-gel"-technology allows a lot of additional surface properties without damaging the receiving glassy surface. In this way:

a) a glassy surface (window glass, mirror….) preliminarily treated with a TiO_2-based "sol-gel"-layer (hydrophilic), will show a real **anti-fogging effect** (Fig. 1).

Fig. 1

b) a "sol-gel"-layer modified with nanometric mineral pigments, allows to develop coloured transparent layers (majolica effects) (Fig. 2).

Fig. 2

c) a glassy surface can develop **self-cleaning properties** if it has been preliminarily modified by a treatment with a photo-catalytic sensitive "sol-gel"-layer (Fig. 3).

Fig. 3

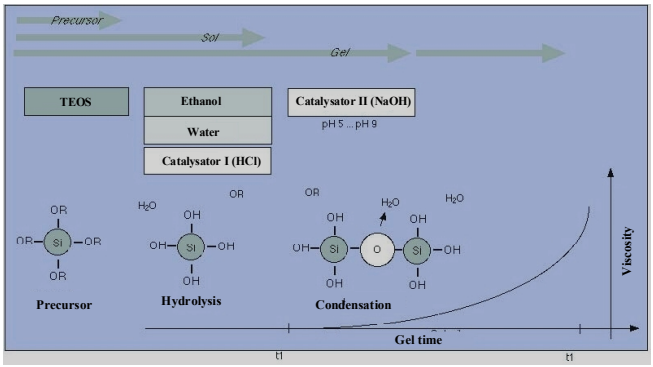
As the glass industry was precursor in the technology, most of the examples have been borrowed from it; however this does not mean that other industries like those of ceramic, paint, cement, ink or porcelain enamels are not involved in the field.

3. What is meant by "sol-gel"-coating?

- A **"sol-gel"-coating is a nano-thick layer**, bonding on glassy surfaces, which is either improving one or more of its properties or giving it one or more additional properties.

- Those layers are generally obtained by "sol-gel"-technology; a technology, which enables the **transformation of molecular precursors reacting with water into oxide materials** and that through a **"sol"-phase** (colloidal) and a **"gel"-phase** (solid material, of which the pores are containing a liquid phase).

The opposing scheme is showing the transformation of the precursor TEOS (= tetra ethoxy silane), which passes from a "sol" state into a "gel" state by means of a hydrolysis and condensation reaction in the presence of ethanol, water and catalysts.



Transformation of the precursor TEOS from a "sol" state into a "gel" state.

- Those **reactions are generally complex** and many parameters, like **the type and concentration of the precursor**, the concentration water-precursor, **the type of catalysts** (acid-base), the **pH value**, the type of used solvent, the temperature, the additives…etc… need to be considered. So a **basic environment** is leading to a **particle increase** and an **acid environment** to a **three-dimensional network evolution of the particles.**

4. A few important points concerning "sol-gel"-layers

- The solutions of "sol-gel" are generally **transparent liquids.**

- **Their application is highly versatile**; based on the form of the piece to be coated, they can be applied **by spraying**, **dipping**, **flow coating**, **spin coating**, **roller coating** or **silk-screening.**

- Independently from the used application method, the applied **layer thickness** is varying between **5 and 8 nanometres** in 1 pass; this implies that **"sol-gel"-layers** are generally **transparent**. Higher thicknesses are achievable by repeating the application and drying steps several times.

- **The bond** of "sol-gel"-layers on a glassy surface is **chemical** and can be explained by the **OH^- -groups** available on the glass, ceramic or porcelain enamel surface. This implies that **the more a glassy surface is hydrophilic** (rich in OH^- -groups)**,** consequently free of grease, dust or other residues, **the more the bond of the "sol-gel"-film** to that surface **will be intense**.

- The **porosity of the "gels"** can be **extremely important**; "gels" can receive in their pores nanometric materials, which can be chemically bound or not to the"gel"-matrix and be at the **origin of multi-functionality**.

Those nanometric additives can be organic or mineral. In case of organic additives, the gels turn into a hybrid material (**ORMOCER = Organically Modified Ceramics**) (Fig. 4).

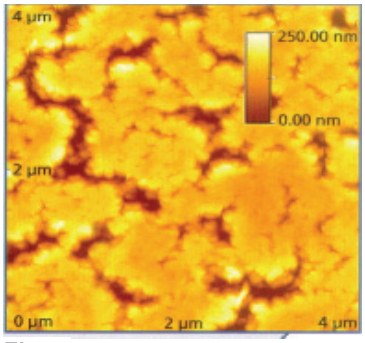


Fig. 4

- The "sol-gel" layers sometimes need to be densified (abrasion or corrosion improvement). This will be possible through an **"annealing process"** at 400-500°C.

5. "NanoClean"

Based on previous considerations and knowledge, has been created:

"NanoClean"

A **"sol-gel" layer, organically modified, which enables the enamelled surfaces to obtain anti-stick properties.**

5.1 *NanoClean / its structure* (Fig. 5)

As outlined below, **"NanoClean" is a silica-based gel, doubly modified,** whose easy-to-clean properties and optimal abrasion are originating from the **molecular organisation that takes place during the polymerisation process** (curing).

The particularity of "NanoClean" is also that **its polymerisation (curing) takes place at room temperature,** which is a real advantage for the user but which can also limit it in its properties (porosity).

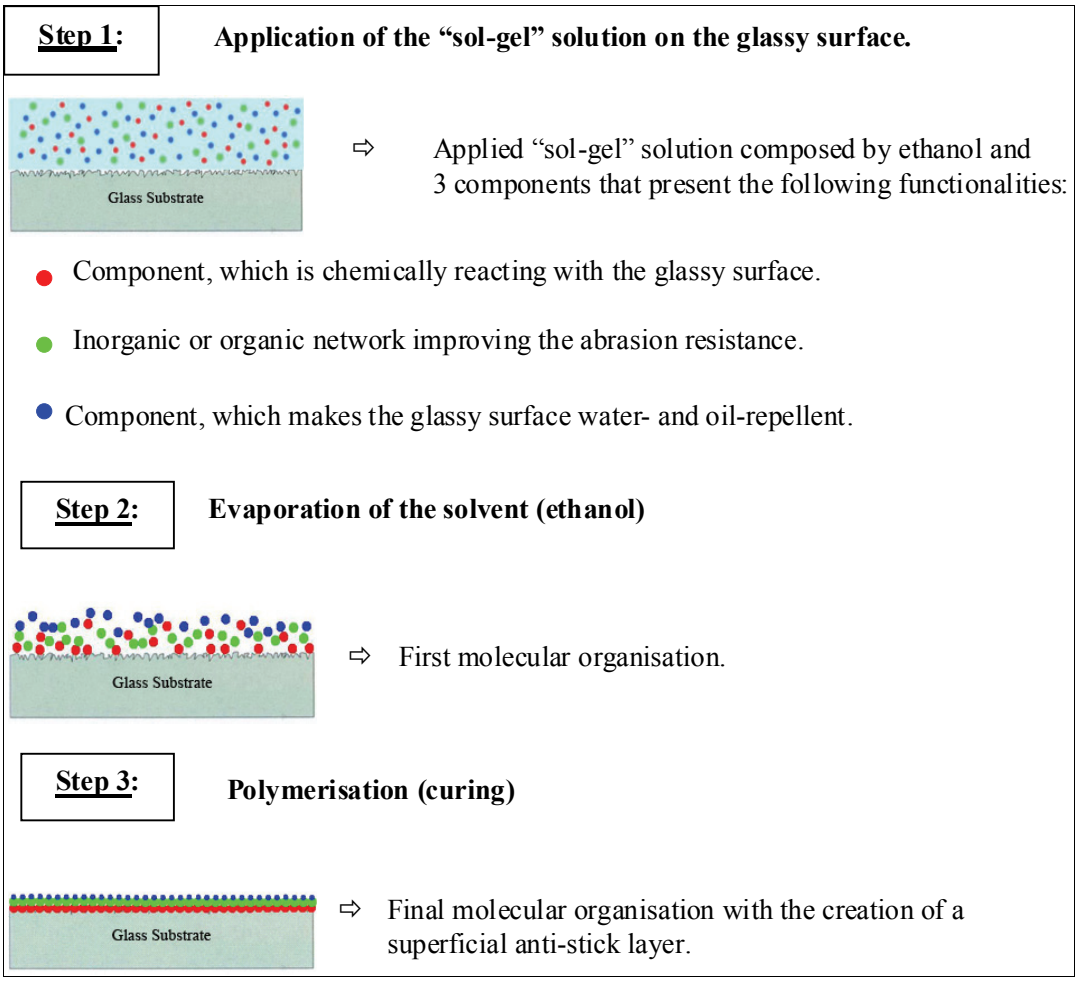


Fig. 5 NanoClean structure

5.2 *NanoClean / its action* (Fig. 6)

NanoClean **changes the surface properties**:

- a **hydrophilic surface** is changing into a **hydrophobic / oliophobic surface,**
- the **high surface energy** into a **low surface energy** and
- the **smooth surface** into a **nano-rough** surface.

These changes result in the fact that the **OH^--groups available at the glassy surface**:

- **(Figure A)** are **reacting with the dirt residues** and lead to a firmly adhering soil crust.

- **(Figure B)** are **reacting with the "sol-gel"-layer**, creating **a barrier against the formation of adhering soil crusts (easy-to-clean effect).**

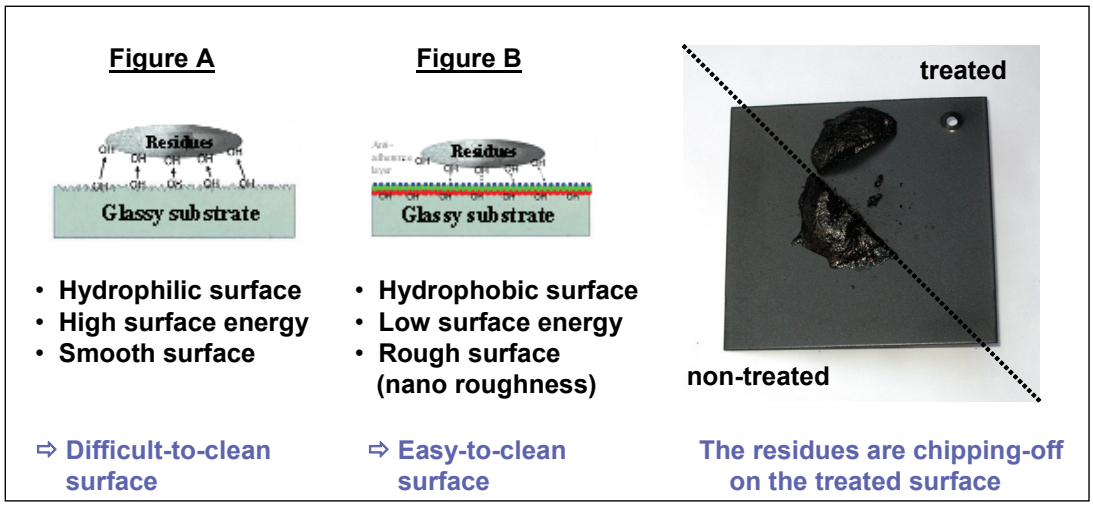


Fig. 6 NanoClean action

5.3 *NanoClean / surface roughness* (Fig. 7)

As already mentioned, it concerns a **nano-roughness** and therefore it is **neither visible nor tangible**.

The graphs below depict the through **AFM** measured roughnesses for a non-treated and with "NanoClean" treated surface.

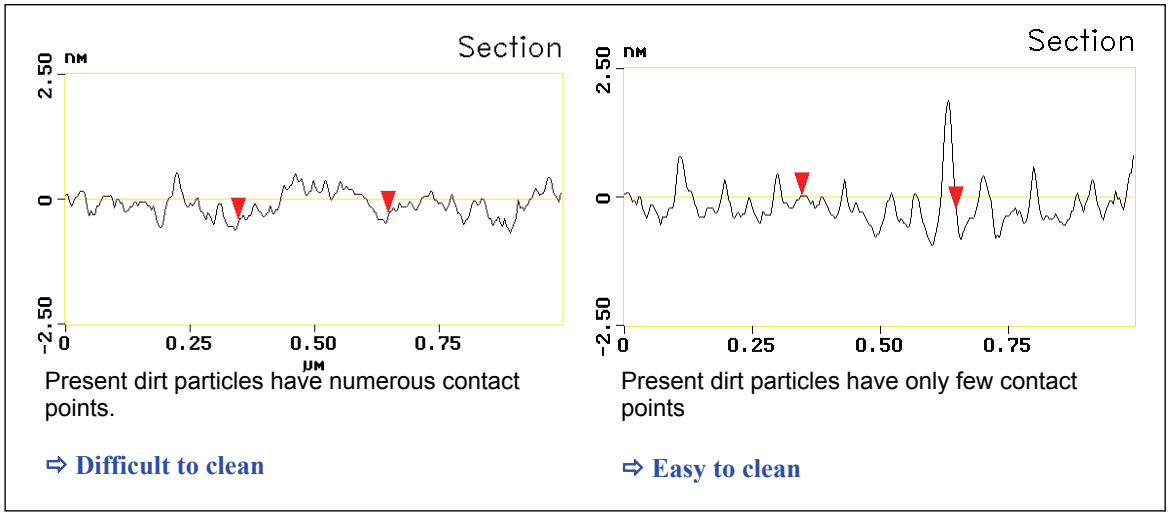


Fig. 7 NanoClean surface roughness

5.4 *NanoClean / Hydrophoby and oliophoby definition / Contact angle* (Fig. 8)

The most important criteria for an easy-to-clean surface are its hydrophoby and oliophoby. These 2 properties that are the keys to an easy-to-clean surface, can be defined through respectively **the contact angle realised by a water drop and a hexadecane drop.**

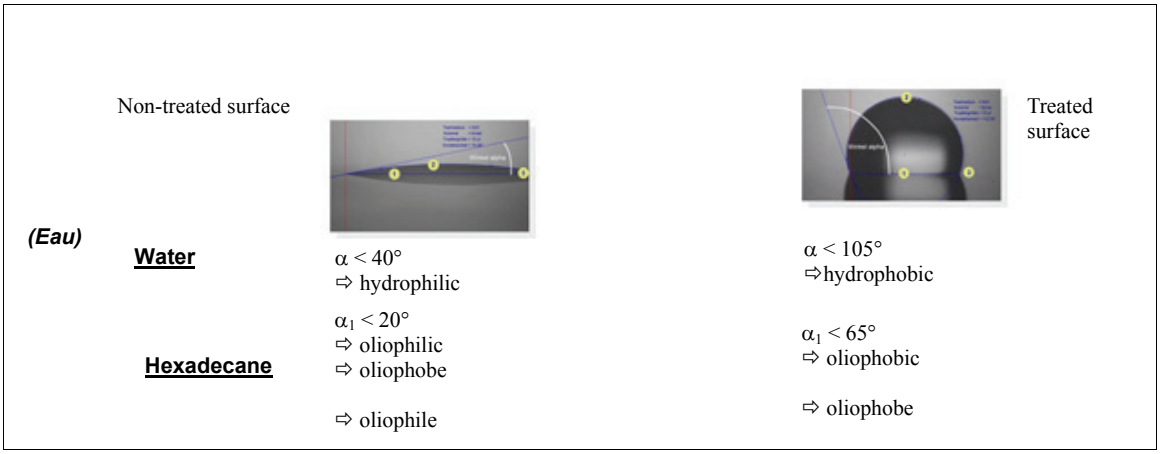


Fig. 8 NanoClean - Hydrophoby and oliophoby definition / contact angle

5.5 *NanoClean / Preparation of the enamelled pieces to be treated*

- Our investigations show that the more the surface to be treated is hydrophilic, the higher will be the bond between the sol-gel layer and that surface.

- This implies that **a surface to be treated needs to be free of grease, dust and other residues.**

- **This is the case for enamelled parts just fired**; their contact angle is generally not higher than 20° but it will fast increase through the deposition of microscopic dust, limiting the OH^- - groups on the enamelled surface and at the same time the capacity of the latter to react with the sol-gel layer.

- In case of **enamelled parts, only stored for some days**, it is preferable **to preliminarily degrease them** using a **degreasing agent free of tensides.**

- In case of **enamelled parts, stored for a longer time (weeks, months),** it is advisable after a degreasing step, **to activate them** through **a light pickling step or a silanisation** operated by "flame spray".

5.6 *NanoClean / Application process* (Fig. 9)

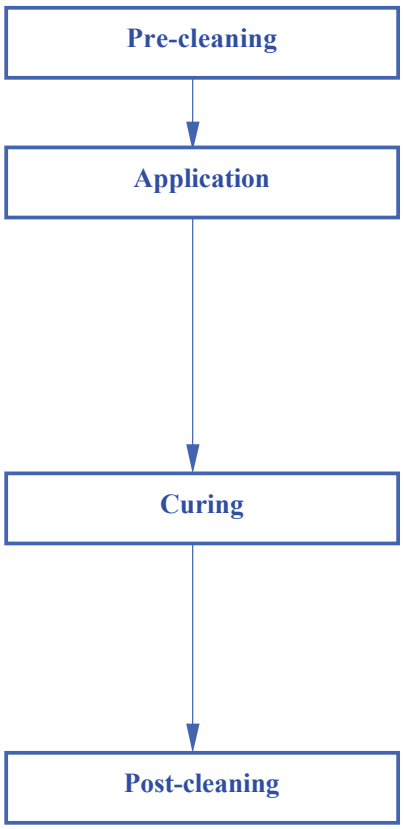
Below the schematic depiction of the different process steps to safeguard an optimal application.

5.7 *NanoClean / Easy-to-clean tests*

The cleaning tests being generally customer-specific and often highly subjective in their evaluation, forced us to chose 2 normed tests and in particular the AHAM-test (USA) and the FAN-test (F), both based on the elimination of baked-on food residues.

5.7.1 *AHAM test*

- The test is based on the fact that a mixture of 9 different foods (ground beef; grated "Cheddar" cheese; homogenised whole milk; powder sugar; cherry juice; instant tapioca; 1 raw egg; flour; tomato juice) is baked onto an enamelled surface. This mixture can be removed more or less residue-free through defined cleaning processes.



- The glassy surface to be treated has to be **perfectly clean** and free from dust and grease (fingerprints) (see previous paragraph).

- There exist different possibilities:
  - by rubbing with the "sol-gel"-solution impregnated cloth (microfibre cloth to avoid fluffs).
  - by dipping in the "sol-gel"-solution (for pieces with a simple form).
  - **by aerosol-spraying** (for pieces with a complex form)**.**
  - by roller-coating or by silk-screening (only for flat surfaces).

- Can be divided into 2 steps:
  - the **initial curing**: 10 minutes at room temperature or 2 minutes at 80°C.
  - the **end curing**: after 24 hours.

  (Please note that the treated surface can be handled after the initial curing).

- The necessity of the last step highly depends on the chosen application (excess of coating material).
  process and application conditions (excess of solution).

Fig. 9 Application process NanoClean

- Procedure:
  The enamelled surface (plate 10 x 10 cm) is soiled on a surface of about 12 cm^2 (4 x 3 cm); the in this way prepared plate is installed on a steel wire grid in the middle of a baking oven. The baking cycle consists of a temperature increase of 20 up to 205°C, followed by a pause of 1 hour. The cooling of the plates is occurring at room temperature.

- Cleaning of the surface:
  The cleaning is occurring with the help of a plastic scraper (A), a plastic scouring pad (B) or a metal scouring pad (C) (copper or steel).

- Evaluation of the cleaning grade:

0	= no residues	0%
1	= a small amount of residues	10%
2	= a few residues	25%
3	= average residues	50%
4	= a lot of residues	75%
5	= all residues are remaining	100%

- Results of the tests:

Cleaning means	A Plastic scraper							B Plastic scouring pad								C Copper scouring pad							
Number of AHAM cleaning cycles	1	2	3	4	5	45	73	1	2	3	4	5	45	79	85	1	2	3	4	5	45	94	96
1. Standard black enamel	4	4	5	5	5	/	/	4	4	4	4	4	/	/	/	1	1	1	1	2	/	/	/
2. Black enamel treated with NanoClean	0	0	0	0	0	0	1	0	0	0	0	0	0	1	/	0	0	0	0	0	0	1	/
3. Standard grey enamel (poesta)	3	3	5	5	5	/	/	3	3	4	4	5	/	/	/	0	0	1	1	2	5	/	/
4. Grey enamel treated with NanoClean	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1
5. PTFE	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1

Explanation

* **The black enamel could be fully cleaned during 72 cycles with the plastic scraper, during 78 cycles with the plastic scouring pad and during 93 cycles with the metallic scouring pad. Afterwards some residues remained on the plates.**

* **Both the grey enamel and the PTFE present more or less a similar cleanability.**

Residues

0 = 0 % Easy-to-clean
1 = 10 %
2 = 25 %
3 = 50 %
4 = 75 %
5 = 100 % Difficult-to-clean

Conclusion:
NanoClean presents anti-adherent properties similar to PTFE.

As previously shown, the coating "sol-gel" **NanoClean** is as for its cleanability similar to PTFE, with **the notable difference that it cannot be visually damaged by kitchen utensils** (knifes or forks).

5.7.2 *Test FAN*

- Like the AHAM test, it is based on the elimination of the residues of foodstuffs left behind on the enamelled surface: milk + salt; meat extract (Viandox – Maggi); lemon; egg; ketchup (Heinz).

- Procedure:
  The previous foodstuffs are applied on a cold enamelled plate.
  1 gr. of each foodstuff is individually put in a stainless steel ring fixed on the enamelled plate by means of a silicone-based adhesive. The in this way prepared enamelled plates are put in a hot-air baking cavity; the baking cycle will take 30 minutes at a temperature of 280°C ± 10°C. The cooling of the plates will occur naturally.

- Cleaning of the soiled plates:
  The plates are preliminarily cleaned with a sponge and warm water (40°C).
  The remaining residues will be eliminated by going 3 times back and forth with an abrasive scouring pad (type VILLEDA Graffix) while exerting an increasing pressure.

- Evaluation of the cleanability grade:

  If the residues are eliminated at:
  * low pressure (1 kg) note : 5
  * average pressure (3 kg) note : 4
  * high pressure (5 kg) note : 3
  * high pressure + detergent note : 2

  If the residues cannot be eliminated at :
  * high pressure + detergent note : 1

  Consequently the note can be contained between 5 and 25.

- Results:

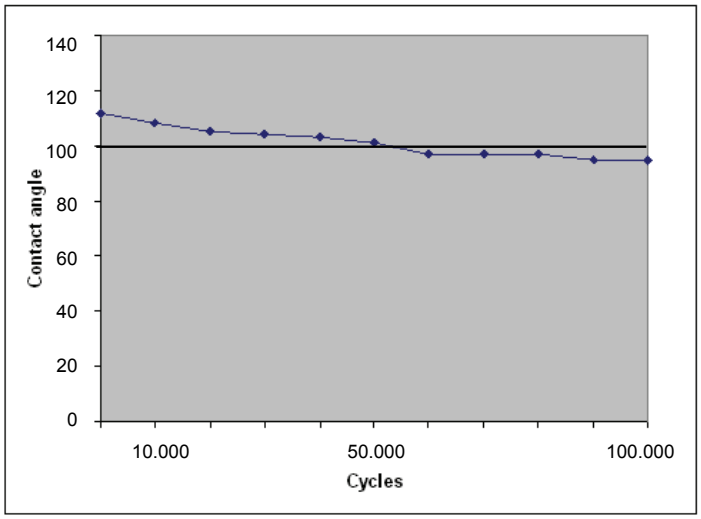
Food-stuffs	Milk + salt	Meat extract	Lemon	Egg	Ketchup	Grade of cleanability
Grey enamel poesta	1	5	2	2	1	11
Grey enamel treated with NanoClean	3	5	5	4	5	22
PTFE	4	5	5	5	4	23

Like the AHAM test, the FAN test is giving similar results: a **NanoClean-coated** enamel is proposing **similar anti-adherent properties** like PTFE.

5.8 *NanoClean / Its properties*

"NanoClean" does not change the properties of the enamelled surface on which it has been applied; on the contrary, it generally improves them or gives them additional properties, like:

- **being optically neutral: "NanoClean" does neither change the colour, nor the surface aspect.**



Rubbing cycles	Contact angle
0	112°
10.000	108°
20.000	105°
30.000	104°
40.000	103°
50.000	101°
60.000	97°
70.000	97°
80.000	97°
90.000	95°
100.000	95°

Fig. 10 Results of the tests

- It proposes **a high scratch and abrasion resistance**, as shown in the graph below (Fig. 10), which illustrates the low **loss of hydrophobic grade (contact angle)** in function of the number of exerted abrasion cycles (max. 15% of hydrophoby loss after 100.000 rubbing cycles) (exerted power : 1 kg / 1 cycle = 1 back – forth).

- By enriching the surface with SiO_2, it increases the **acid resistance** and it intervenes neither positively nor negatively in the alkaline resistance.

- It presents **exceptional "anti-stick" properties** through its high hydrophobic and oliophobic grade.

*** hydrophobic grade : > 100°**

*** oliophobic grade : > 60°**

- It is **temperature-resistant up to maximally 300°C** (in particular when the surface has been pre-silanised); on the contrary, it is fully destroyed at higher temperatures, however without leaving any visible traces; it **can be regenerated** by using a **NanoClean Duo Set** (Fig. 11) and by following a well-defined procedure.

Fig. 11 NanoClean Duo Set

- It also proposes a **good UV-resistance** (particularly interesting in case of glass coatings), it **is environmentally friendly** and is **food-neutral (food approval certificate)**.

5.9 *NanoClean / Some practical information*

- NanoClean is a **2-component "sol-gel" system** :
  1 basic solution + 1 activator

- The **mix of both forms the "NanoClean" solution**, which can be stored during 2 weeks (15 days).

- The basic solution can be stored during **2 years**, the activator during 1 year.

- Based on the method of application, the NanoClean solution is applied at **10 to 15 ml/m^2**.

5.10 *NanoClean / Cost impact*

- Based on the overspray, the additional cost is varying between 1,20 and 1,80 €/m^2.

6. Conclusion

Like all other coatings on the market, “sol-gel”-coatings present advantages and disadvantages:

- **among the advantages, we can note** :
  - the numerous **possibilities of surface properties modifications** (anti-stick; anti-fogging; photo-catalytic; UV-protection; electrically conductive…etc…).
  - the **simplicity and versatility of application** (if the substrate has been prepared correctly).
  - The low **energy, which is required to cure** the “sol-gel” layers (from room temperature up to 400-500°C).
  - The possibility to be **regenerated**.

- **among the inconveniences, we can note** :
  - the reduced mechanical properties through the nano-thickness of the layer.
  - the required thorough pre-cleaning (if the coating is not realised immediately after firing).

Nevertheless the “sol-gel” layers remain in our opinion **one of the most interesting future-directed ways to supply the glassy surfaces** and especially the porcelain enamels with specific functional additional properties.

“NanoClean” is illustrating this very well through the change of a simple enamel surface into an easy-to-clean surface and is for that purpose using the same principle as in nature, where dust is dripping from the leaves and flower surface.