


# HYGIENIC COATINGS


## Easy to Clean Nanocomposite Metal Coatings for Food Processing

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## Abstract

Cleaning and keeping clean of food processing equipment is of extremely high importance for hygienic reasons and, in many cases, also a cost factor for the whole process. Various low surface free energy coatings have been developed which show an antiadhesive behaviour to grease or food components, such as mustard, ketchup or fruit juices, even if baked at elevated temperatures on the coating surface. These coatings are composed of sol-gel derived hybrid materials, ceramic nanoparticles for mechanical stabilization and fluorinated silanes. By appropriate processing, gradient coatings with stable low surface free energy are formed. The coatings are stable up to 300°C and have been tested for kitchens stoves, chip-pans and other kitchen appliances. These coatings also show a great application for other fields in food processing, the dairy industry, meat processing, bakeries or breweries, where essential savings in cleaning costs were estimated.

## Introduction

Surfaces, which come into contact with food at elevated temperatures in many cases are difficult or even impossible to be kept clean, if baked or burnt food residues remain on the surface. The cleaning effort to remove this food rests causes time and costs in food industry. The cleaning effort can be diminished, if the adhesion of food on the surface can be kept low even after a baking process at higher temperatures. One way to approach this problem, especially for baking devices, is to employ perfluorinated polymer coatings like PTFE, which show an excellent antiadhesive effect. However, these polymers are soft, not transparent, relatively thick and have a maximum application temperature of 250-300°C [1,2]. Moreover due to the antiadhesive property of the bulk material, often adhesion problems of coatings made from these materials occur. To get a satisfying adhesion, in most cases an adhesion layer is necessary.

Another possibility to solve the problem of food adhesion are coatings made from sol-gel based hybrid materials. As shown in [3,4], coatings made from these materials can be functionalised to antiadhesive films by incorporation of silanes with perfluorinated side chains. Additional functions have been incorporated by other

functional groupings or oxidic or metallic nanoparticles [9]. As shown in [5,6,10] the fluorinated or alkyl side chains cause a gradient formation during drying leading to an upconcentration of fluorinated chains at the surface. Nanoparticles bound to the network improve the mechanical resistance of the coatings. Nanocomposite materials with antiadhesive function have been developed for applications like easy clean coatings on sanitary wear or for the printing industry [7].

In this paper the influence of different functional groupings (fluorinated or alkyl side chains), on the surface free energy and the scratch resistance of coated metal surfaces are described.

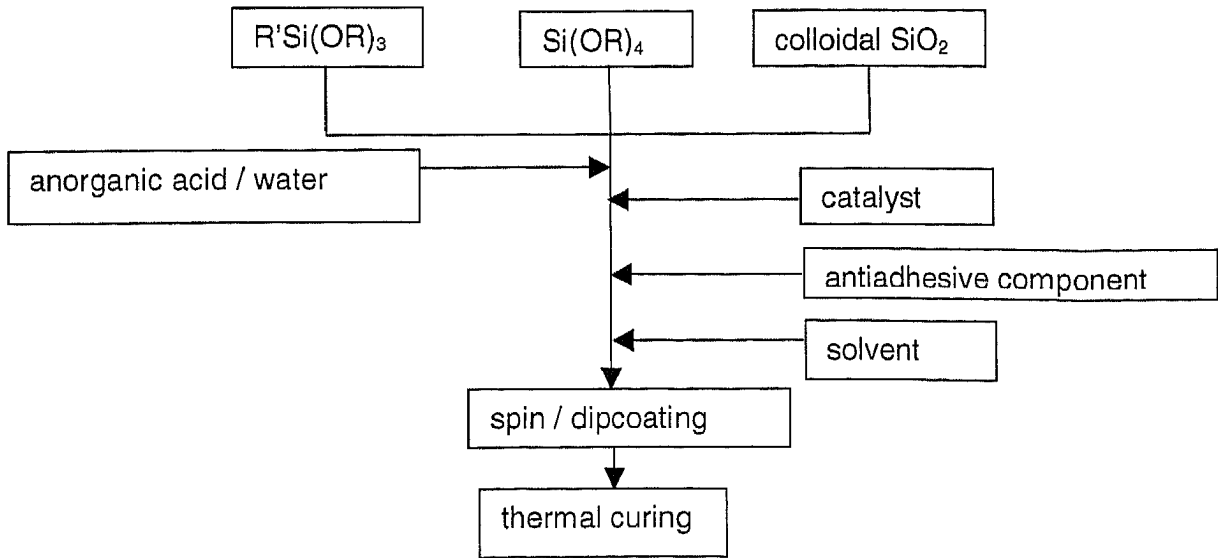
The coating has to resist chemical-, thermal- and mechanical impacts. To improve the inorganic backbone formation, the influence of different condensation catalysts ( $Zr(OBu)_4$ ,  $Zr(OPr)_4$ ,  $NaOH$ ) on the material properties has been investigated. The durability as a function of food contact as well as the contact angles of the modified materials are examined.

The described transparent coating materials show a good wetting and adhesion on chromium and stainless steel substrates and can be easily applied via conventional coating techniques like spraying or dip coating.

**Experimental**

The coating materials were synthesized from tetraalkoxysilane, alkytrialkoxysilane and silica sol with different antiadhesive acting alkoxides, according to the general scheme shown in figure1.

**Figure1: General synthesis scheme of the low energy coating material**



The systems were obtained via sol-gel reaction by controlled hydrolysis and condensation.

Zirconium alkoxides and NaOH have been applied in the following quantities:  $Zr(OBu)_4$ , 7,5 mol%;  $Zr(OPr)_4$ , 6 mol%; NaOH 15 mol%. For testing, stainless steel and chrome plated steel, sheets have been used. The sheets were cleaned by an alkaline detergent bath at 70°C and an ultrasonic treatment. Spray- and dipcoating were used as coating process (solid content 15 wt%, solvent 2-propanol). The curing was carried out at 350°C for chromium substrates and 300°C for stainless steel substrates.

The surface free energy of the coatings was determined by contact angle measurement and following calculation according to the method of Wu [8].

The scratch resistance was investigated by scratching the surface with a vickers diamond tip and monitoring the loading, at which the first visible damage (observed under the microscope) occurs. The abrasion resistance was determined by the Taber Abrader testing method, according to ISO 9352.

The chemical resistance is tested by immersing the sheets in boiling ketchup/water/table salt mixture (50%) for 15 minutes or to oil, heated to 200°C for 1h. After cleaning and drying the substrates, the contact angle against water and hexadecane was measured.

The thermal resistance was determined by storing the surfaces in an air-circulating drying oven at different temperature/time conditions (15min/400°C, 30min/400°C, 24h/350°C).

## **Results and Discussion**

### **1. Antiadhesive Properties**

As shown elsewhere [10] an upconcentration near the surface takes place in general. Using zirconates as condensation catalysts, it was of interest whether this effect can be maintained or whether the silane is irreversibly united to the backbone. In table 1 the results of the examinations, obtained from various compositions are shown. In order to examine the influence of different antiadhesive groupings on the easy to clean effect various organoalkoxysilanes were used. They differ by the number, length or constitution (C-H, or C-F bonds) of the functional side chain (table 1). In addition to this the intention was also to use compounds with thermal stable side chains. It was supposed that shorter hydrocarbon chains should be more stable.

The material is applied by spray coating on smooth chromium sheets and cured at 350°C for 30 minutes. The surface free energy of the coatings, which is calculated from the contact angles of specific solvents with known surface tension, is to a certain degree a measure of the adhesion of contaminations and the degradation of the coating during the food baking process. The following table compares the surface free energies and the scratch test results of the investigated materials and the uncoated substrate.

**Table1: Comparison of uncoated chromium and 4 nanocomposite coatings, which differ by the antiadhesive component (8,7 mol%).**

<b>material components</b>	<b>contact angle (water / hexadecane) [°]</b>	<b>surface energy [mN/m]</b>	<b>scratch test [g]</b>
Chromium uncoated	56 / 10	42	1
M1: R'Si(OR) <sub>3</sub> , Si(OR) <sub>4</sub> , SiO <sub>2</sub> , Me <sub>2</sub> Si(OR) <sub>2</sub>	84 / 38	25	4
M2: R'Si(OR) <sub>3</sub> , Si(OR) <sub>4</sub> , SiO <sub>2</sub> , Me <sub>3</sub> Si(OR)	92 / 43	23	3
M3: R'Si(OR) <sub>3</sub> , Si(OR) <sub>4</sub> , SiO <sub>2</sub> , (R'O) <sub>3</sub> Si-(CH <sub>2</sub> ) <sub>3</sub> -CF <sub>3</sub>	90 / 32	24	3
M4: R'Si(OR) <sub>3</sub> , Si(OR) <sub>4</sub> , SiO <sub>2</sub> , (RO) <sub>3</sub> Si-(CH <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> F <sub>13</sub>	104 / 63	15	3

The results demonstrate, that all compositions show a relatively low surface free energy. Taking into account the low content of organoalkoxysilanes, it can be concluded, that the enrichment of the hydrophobic groupings also takes place within the investigated systems. The nanocomposite coatings M1 - M4 show distinctively lower surface free energy values, than the uncoated metal substrate. The surface free energy values of the coatings with alkyl and with short polyfluorinated side chains (M1 M2, M3) are similar. In contrast to these values the material M4 with long F-side chains, shows the lowest surface free energy, which implies a good antisoiling

effect. In spite of the elevated temperatures (350°C) the stability of the longer F-chain component is high enough and the resulting hydrophobic and oleophobic effect of the coating remains untouched. M4 with the longest perfluorinated side chain shows the lowest surface free energy.

The mechanical resistance of the coatings, as derived from the scratch tests, has improved compared to the uncoated metal surface. The dimethyl functionalised silane containing nanocomposite shows the highest scratch resistance.

## 2. Effect of the condensation catalyst

The following investigations deal with the influence of condensation catalysts on chemical, thermal, and mechanical resistance of the nanocomposite coating. A composition ( $R'Si(OR)_3 / Si(OR)_4 / SiO_2 / (RO)_3Si-(CH_2)_2-C_6F_{13}$ ) was chosen for these investigations, because the long chain perfluorated alkoxide, which shows the best performance of coating functionality, was used as antiadhesive component. The material was applied by dip-coating on stainless steel sheets because of its easier wetting behaviour compared to chromium.

As shown in table2, Zirconium n-butylate, zirconium n-propylate and sodiumhydroxide are introduced to the coating system, which is cured at 300°C. Zirconium alkoxides are employed because earlier investigations prove their enhancement of chemical stability for easy-to-clean nanocomposite coatings. This corresponds to examinations of glasses whose chemical resistance also could be improved by incorporating zirconium alkoxides [11].

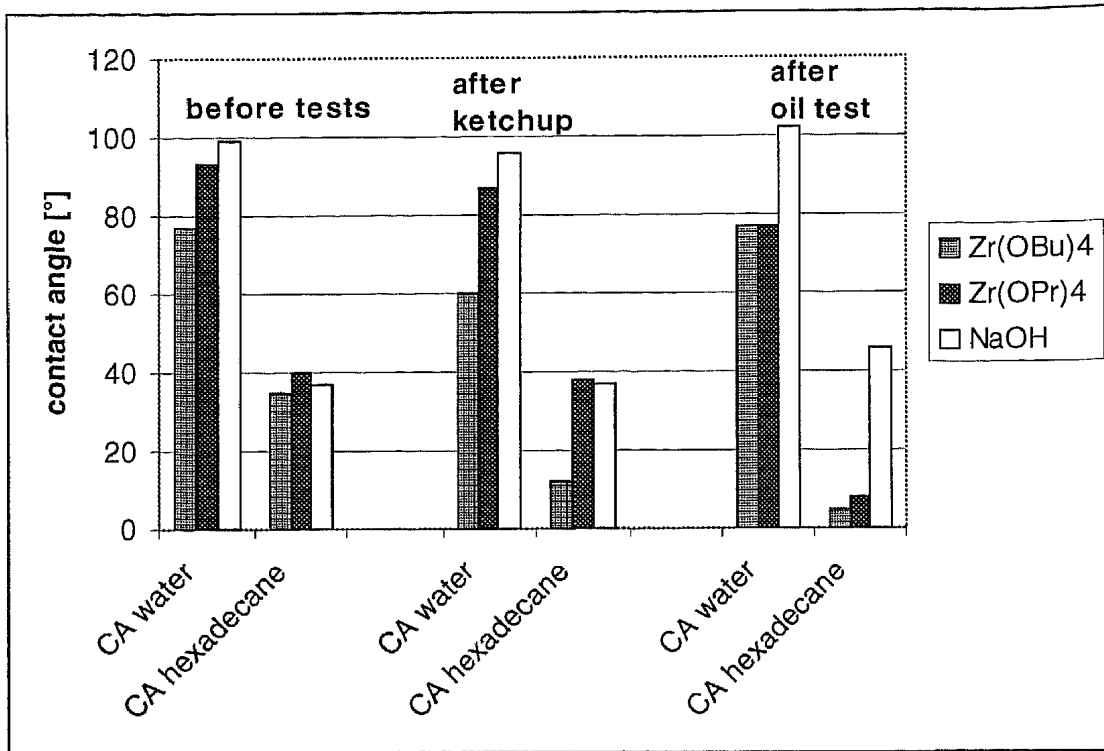
**Table2: Composition of the investigated materials**

material	components	catalyst [mol%]
M5	$R'Si(OR)_3 / Si(OR)_4 / SiO_2 / (RO)_3Si-(CH_2)_2-C_6F_{13} / Zr(OBu)_4$	7,5
M6	$R'Si(OR)_3 / Si(OR)_4 / SiO_2 / (RO)_3Si-(CH_2)_2-C_6F_{13} / Zr(OPr)_4$	6
M7	$R'Si(OR)_3 / Si(OR)_4 / SiO_2 / (RO)_3Si-(CH_2)_2-C_6F_{13} / NaOH$	15

The contact angle of water and hexadecane are determined on the untreated surface of the coatings. Afterwards the coatings are submitted to two food test substances

(test1: cooking ketchup mixture; test2: edible oil at 200°C). After cleaning the surfaces, the contact angles are measured again. The following figure demonstrates the contact angles before and after the contact with ketchup or oil.

**Figure2: Water and hexadecane contact angles of nanocomposites synthesized with different condensation catalysts ( Zr(OBu)<sub>4</sub>, Zr(OPr)<sub>4</sub>, NaOH), before and after ketchup and oil test**



Compared to the other systems, the chemical resistance of the Zr(OBu)<sub>4</sub> is low. This may be explained by the lower catalysing effect of the Zr(OBu)<sub>4</sub> due to the sterical hinderance of the butyl groups and their positive inductive effect. Additionally a remarkable decrease of the hexadecane contact angles after both food tests can be recognized, indicating that the fluorinated component is not sufficiently bounded to the network. The reason may be the low water content in the reaction mixture at the time of addition.

The relatively low water contact angle of unstressed material M5 (Zr(OBu)<sub>4</sub> catalyst) shows its lower hydrophobicity. It is assumed, that Zr(OBu)<sub>4</sub>, partly forms areas of ZrO<sub>2</sub>, which have a more hydrophilic character compared to the matrix.

Zr(OPr)<sub>4</sub> catalysed coatings show better chemical stability of the obtained coating than the butyl alkoxide catalysed ones. The contact angles remain at a high level besides the contact angle of hexadecane after oil test. The low contact angle of

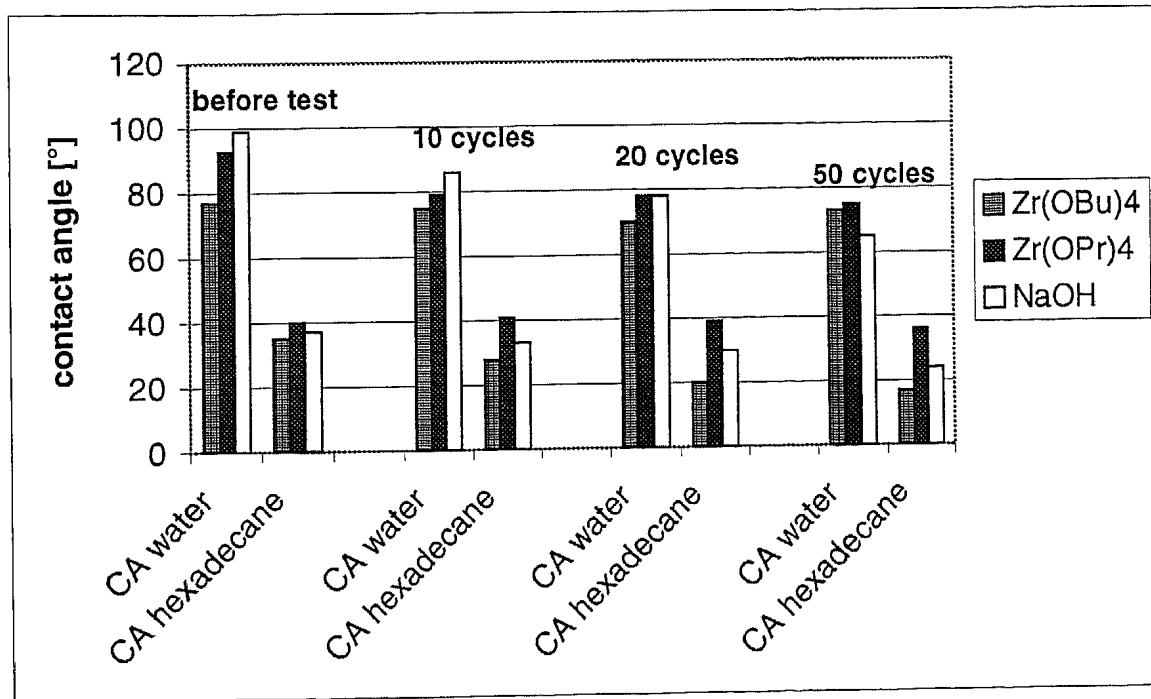
hexadecane after the oil test may be caused by degradation of the fluorinated component at 200°C.

NaOH catalysed coatings show the best chemical resistance in this comparison. No influence on the hydrophobicity and oleophobicity of the surface by the food tests can be determined. The mechanism of the NaOH catalysed condensation is different from the others. Due to higher condensation rates at high pH values, the reaction in alkaline medium seems to lead to higher degrees of condensation.

### 3. Mechanical Stability

The mechanical stability of the compared nanocomposites are tested by a Taber Abrader Test (ISO 9352). The contact angles of water and hexadecane are measured before and after 10, 20 and 50 abrasion cycles. Figure3 shows the received contact angles before and after the different abrasion conditions.

**Figure3: Water and hexadecane contact angles of nanocomposites synthesized with different condensation catalysts (  $Zr(OBu)_4$ ,  $Zr(OPr)_4$ , NaOH), before and after Taber AbraderTest.**



$Zr(OBu)_4$ ,  $Zr(OPr)_4$  and NaOH catalysed materials show a steady decrease of contact angles. During the abrasion, the coating is partially worn down, which causes a loss of functionality.

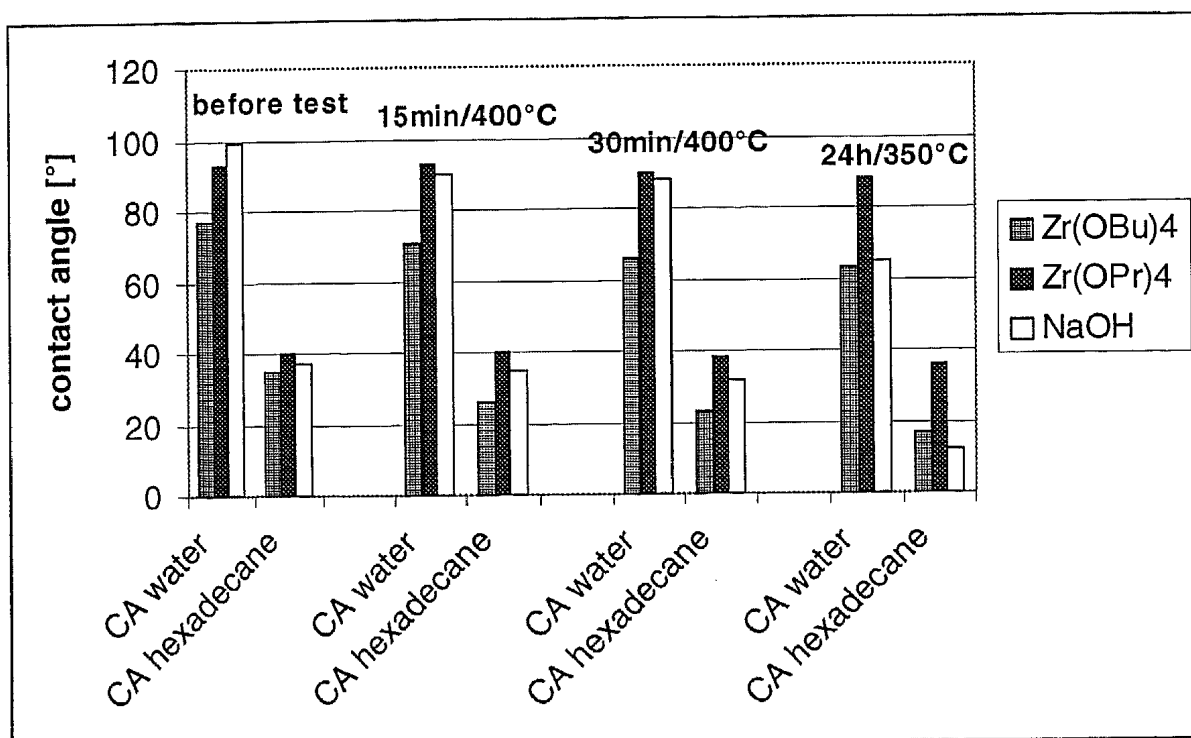


Zr(OPr)<sub>4</sub> shows the lowest influence of hydrophobicity and oleophobicity by the abrasion test. To a certain degree the low surface free energy of the Zr(OPr)<sub>4</sub> catalyzed nanocomposite can be maintained.

#### 4. Thermal Stability

The thermal stability of the compared nanocomposit materials is determined by subduing the samples to three different temperature conditions (15 min/400°C, 30min/ 400°C, 24h 350°C testing of long term stability). Before and after this treatment the contact angles of water and hexadecane are measured, which is outlined in figure4.

**Figure4: Water and hexadecane contact angles of nanocomposites synthesized with different condensation catalysts ( Zr(OBu)<sub>4</sub>, Zr(OPr)<sub>4</sub>, NaOH), before and after thermal impact.**



It can be noticed that, in this comparison of condensation catalysts, the Zr(OPr)<sub>4</sub> material again shows the best results. The contact angles hardly decrease by the influence of temperature even at long term thermal conditions 24h at 350°C. This observation corresponds to the improved chemical resistance of the Zr(OPr)<sub>4</sub> system and the explanations given above. The NaOH catalysed material shows similar good results at short thermal impact, but a slow decrease is already visible. It can be noticed that the functionality of Zr(OPr)<sub>4</sub> and NaOH catalyzed materials decrease with longer times of thermal influence. It is not quite clear how this can be explained, but an alkaline attack on the Si-O-Si bonds (NaOH) may take place.

## Conclusion

Investigations on nanocomposites with tailored functionalities concerning food adhesion, prove to be suitable for easy to clean coatings in the field of food processing.

From different alkoxides with antiadhesive acting side chains the long F-chain alkoxide achieves the lowest surface free energy after introducing to a nanocomposite material, which is cured at a temperature of 350°C.

Based on this system the influence of condensation catalysts ( $Zr(OBu)_4$ ,  $Zr(OPr)_4$ , NaOH) was investigated.  $Zr(OPr)_4$  catalysation leads to a nanocomposite material with improved chemical and thermal resistance. These are useful results in order to fulfill the chemical, thermal and mechanical requirements on surfaces used for food processing. First examinations concerning cell toxicology of the components used in this examinations have been done and turned out to be suitable for food applications. Migration tests still have to be carried out.

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