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BFP ADVANCED TECHNOLOGIES

Designing a facile preparation mode for the development of transparent and durable antisoiling coatings with enhanced anti-static properties

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European Union
European Regional Development Fund

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SPECIAL SECRETARIAT FOR ERDF & CF PROGRAMMES
MANAGING AUTHORITY OF EPAnEK

EPAnEK 2014-2020
OPERATIONAL PROGRAMME
COMPETITIVENESS
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INNOVATION

ΕΣΠΑ 2014-2020
ανάπτυξη - εργασία - αλληλεγγύη
Partnership Agreement
2014 - 2020

Co-financed by Greece and the European Union

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Introduction: Anti-Soiling Coatings

Main Pollution Sources on Indoor & Outdoor Hard Surfaces

Indoor Surfaces

- **Contaminants** (e.g. limescale, dirt, fingerprints, fat, oils, soap scum, remnants of acidic/alkaline cleaners)
- **Biological Pollution** (i.e. mold, fungi, bacteria growth)

Treatment: Anti-Soiling Coating

Outdoor Surfaces

- **Air Pollution** (e.g. industrial waste, exhaust/ woodburning gases, acid rain, biological organisms, pollen)
- **Increased Dust Accumulation** (e.g. desert dust storm)

Treatment: Anti-Soiling & Anti-Static Coating

Types of Anti-Soiling Coatings

Anti-Soiling Coatings

Hydrophilic (mainly titania coatings)

Water droplets spread over the surface and wash away pollutants

- (+) Very good self-cleaning and anti-static properties
- (+/-) Can be highly effective against organic pollution but demand exposure to sunlight

Hydrophobic (mainly silica coatings)

Water droplets roll off the surface carrying away pollutants

- (+) Good water-oil repellent properties
- (+) Functional in both indoor & outdoor applications
- (+/-) Covalently bond to silica surfaces (e.g. glass) but have limited adhesion on non-hydroxylated surfaces (e.g. plastics)

Benefits of anti-soiling and anti-static coatings

- Mitigation of soil & dust,
- Improve overall performance and life-time of expensive applications, i.e. solar panels, CSP, glass buildings, etc.,
- Reduce health, environmental & economical risks

There is an increasing demand for cost effective, enduring coatings that combine the "best of the two worlds", i.e. the anti-soiling behavior of hydrophobic coatings with the anti-static attributes of hydrophilic coatings, within a single multifunctional approach for various substrates

Common Methods to fabricate a Hydrophobic Anti-Soiling Coating

1) Deposition of low surface energy materials

- Organic Materials (e.g. Silicones, Fluorocarbons, Polymeric binders)
- Hybrid Materials (e.g. based on alkoxysilanes)

2) Roughening the surface and deposition of low surface energy materials

Method for the development of superhydrophobic materials, that usually lack durability

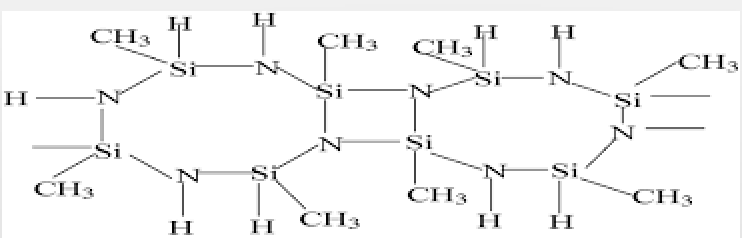
Techniques to fabricate a Hydrophobic Anti-Soiling Coating

- CVD (Chemical Vapor Deposition)
- Plasma Etching
- Self-assembly and Layer by Layer (LbL) methods
- **Sol-Gel Method and Polymerization Reaction**
- Electrochemical Deposition
- Electrospinning
- Lithography
- Wet chemical and hydrothermal systems

Benefits of the Sol-Gel Method:

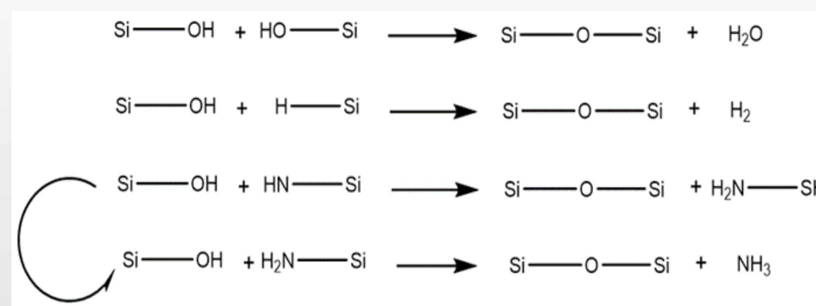
- Flexible method: Facile preparation based on silanes
- Mild processing conditions: Low mixing / curing temperatures, non-toxic materials
- Straightforward procedures, inexpensive equipment, simple application process

The primary materials used in the Sol-Gel Method for the fabrication of functional hydrophobic coatings are the alkoxysilanes.
Polysilazanes (i.e. preceramic materials with alternating silicon and nitrogen atoms) are also widely used for producing thick, hard coatings with barrier properties for various substrates (plastics as well).



Organic Polysilazane(OPSZ)

Both alkoxysilanes and polysilazanes can undergo hydrolysis & condensation reactions when reacting with moisture:



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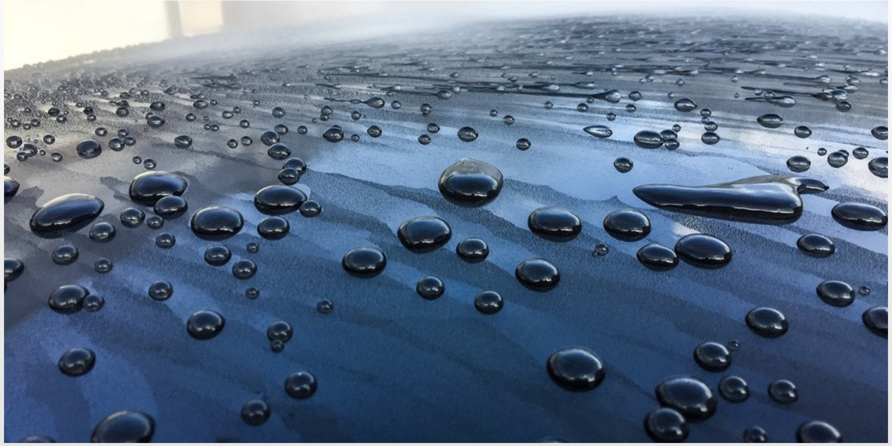
PROPOSED ANTI-SOILING & ANTISTATIC COATING

Features of the Proposed Coating

- Enhanced Hydrophobicity (WCAs of 100-105^{0})
- Anti-Soiling properties
- Anti-Static properties
- Transparency
- Robustness
- Large-Scale applications
- Good adhesion to a variety of substrates



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EXPERIMENTAL PROCEDURE

Materials & Methods

A two-step coating system is examined:

- The first step comprises a primer based on an organopolysilazane (**OPSZ**, Durazane 1500 Rapid Cure by Merck) which can act as a binder. The primer is supposed to provide abrasion and solvent resistance on substrates with medium or negligible amount of hydroxyl groups (i.e. metals and plastics).
- The second step comprises the deposition of a quaternary ammonium silane (**Si-QUAT**, HM4072 by Gelest Inc.) which can co-condense with the underlying OPSZ upon curing and provide anti-soilng and anti-static attributes.
- **Primer Composition:**
  - ✓ 1% wt. of the OPSZ diluted in butyl acetate.

- **Coating Composition:**
  - ✓ 1% of the Si-QUAT diluted in water at pH=3. A non-ionic surfactant (Polyquart Ampho 149 by BASF) at 0,15% was used to improve wetting and drying time.

Application:

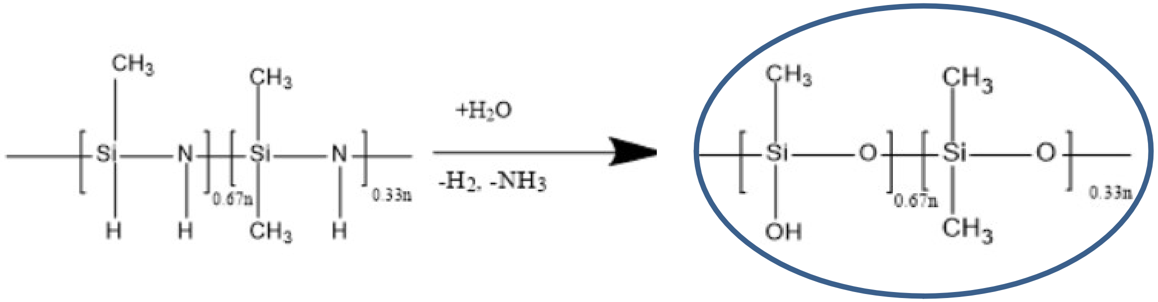
The coatings were applied manually using a clean microfiber cloth on glass, steel and PMMA substrates ($10x10cm^2$). The primer was left to dry for 10 minutes in air. Then the top coat was applied.

Curing time:

7 days at room temperature.

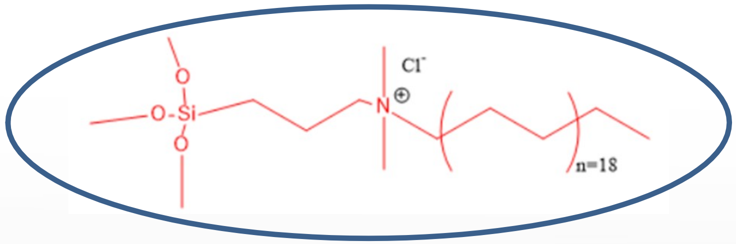
Crosslinking mechanism

- The organopolysilazane and the quaternary ammonium silane reacted with moisture and were hydrolyzed.
- Condensation and polymerization reactions → Formation of siloxane bonds between the primer and the coating.

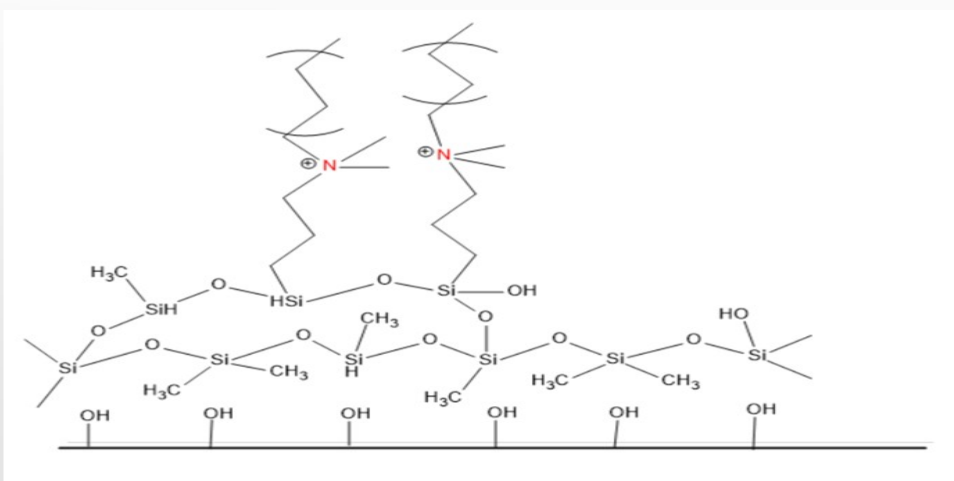


Hydrolyzed OPSZ

+



Si-QUAT



Hybrid Structure of Siloxanes/Polysilazane (thickness ~ 100 nm)

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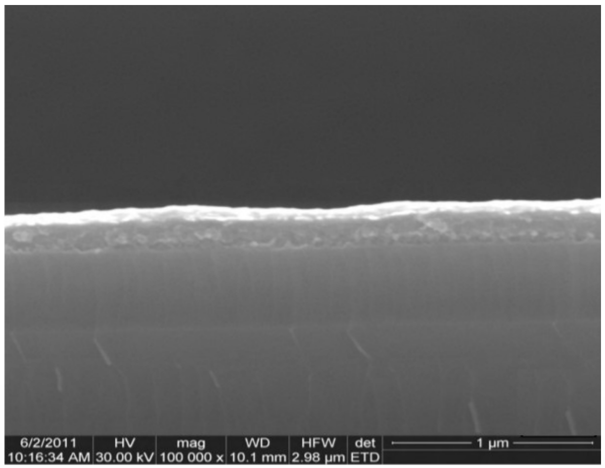
RESULTS

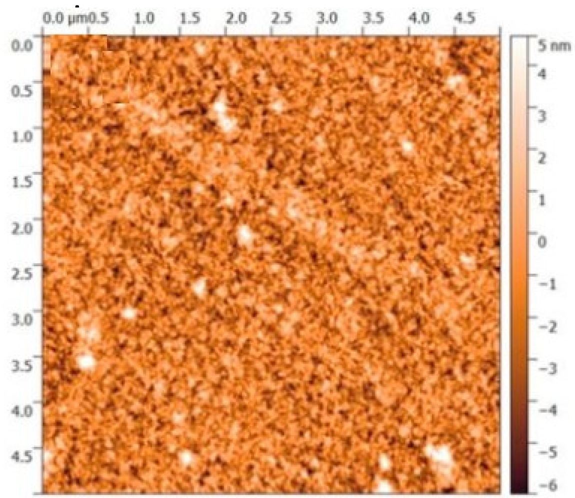
COATING MORPHOLOGY ANALYSIS

SEM cross-section micrograph on coated stainless steel



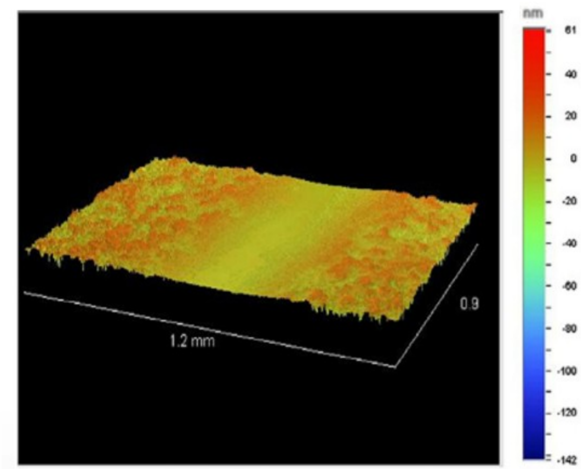
The primer adheres well to the substrate, while the coating presents excellent step coverage. No micro- or nano-voids, cracks, tearing or detachments are observed.

AFM image of the coating on steel



A highly uniform surface topography pattern is observed. The mean surface height is about 5 nm.

Wear track analysis of coated steel samples

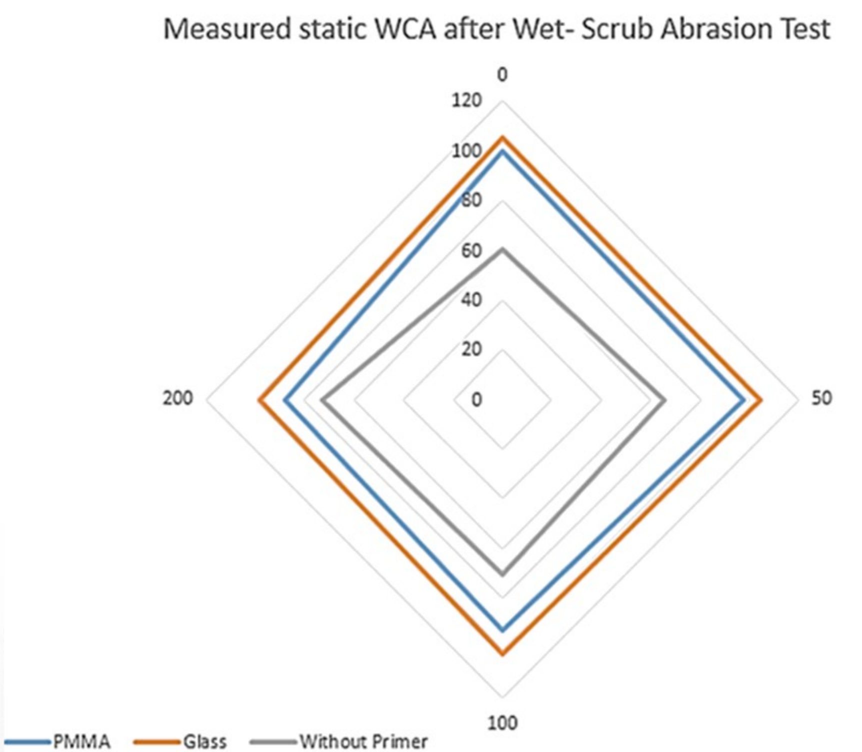


The coating has increased wear strength. The surfactant used has improved the wetting of the OPSZ primer, thus leading to enhanced crosslinking with the Si-QUAT top coat. This process increases surface hardness.

Attachment of dirt becomes harder and self-cleaning is enhanced.

Wet Scrub Abrasion Test According to EN ISO 11998

Abrasion resistance of the coating on glass, PMMA substrates and PMMA substrate without primer.



- **Hydroxylated substrate: Excellent Abrasion Resistance**

Strong crosslinked network between the primer & the topcoat + Strong adhesion of the primer to the glass

- **Non-hydroxylated substrate: Improved Abrasion Resistance**

Very low abrasion resistance without the primer

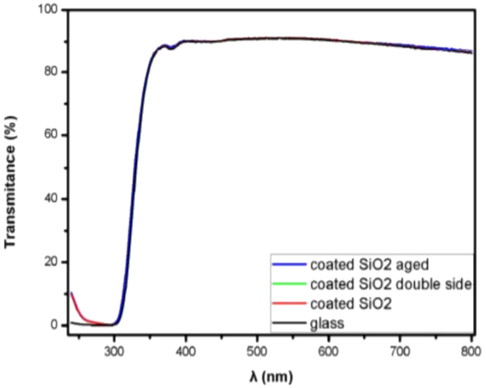
Very good adhesion of the primer on PMMA

Initial WCA:
glass: 40^0
PMMA: 70^0

Silazane-Siloxane Coating System	Static WCA on glass substrates before the abrasion test	Static WCA on PMMA substrates before the abrasion test	WCA after 200 wet scrub cycles on glass substrates	WCA after 200 cycles wet scrub on PMMA substrates	WCA after 200 cycles wet scrub on PMMA substrates without primer
1:1 actives	105°	102°	98°	88°	73°

Laboratory Soil Test on Glass Substrates: Correlation to coating's transmittivity

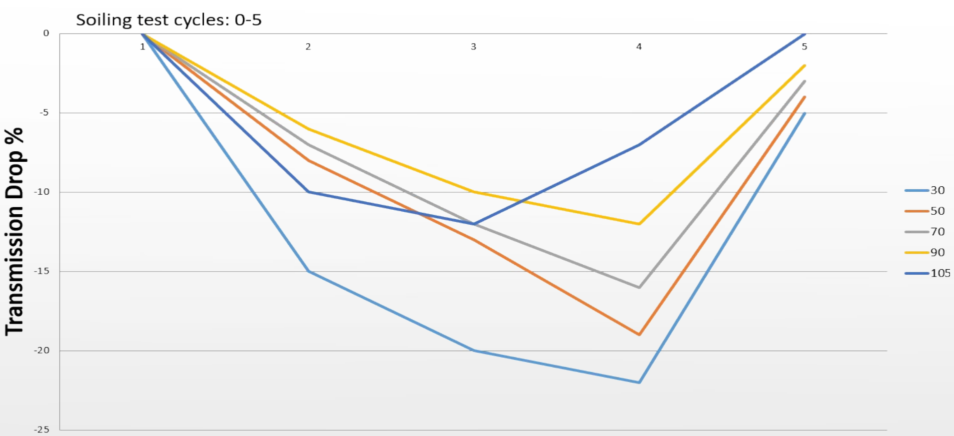
UV-Vis Spectrophotometry results for evaluation of the optical properties of coated glass.



Optical transmittance of uncoated samples was compared to the transmittance of coated samples.

It was found that the incident irradiation penetrated unhindered the coating without any alterations in its intensity. No transmittivity alterations were recorded after aging of the samples (120 hours at 80 ^{o}C).

Correlation of coating's anti-soiling & anti-static properties with its Optical Transmission loss.



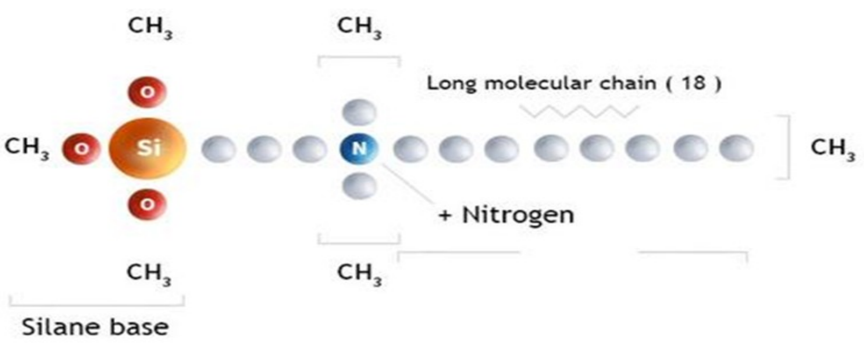
- Five glass coatings with WCA values ranging from 30^{o} to 105^{o} were subjected to 5 cycles of soiling test.
- Each test followed a specific soiling sequence: First the sample was immersed for 5 min in distilled water. Then dust was applied by blowing air. Drying for 24 hours followed. The 1st and 5th cycle additionally included a final step of washing with distilled water for 30 sec.

- The proposed anti-soiling & anti-static coating demonstrates values of WCAs in the order of 105^{o}. In general, hydrophobic coatings with high contact angles performed best.

➢ *It was found that soil accumulation, transmittance and surface energy are strongly correlated*.

The mechanism behind Anti-Soiling & Anti-Static Properties

Structure of Quaternary Ammonium Silane



1. C-18 long Aliphatic Chain:
- Decreases surface tension→ Hydrophobicity
- Exhibits lubricity

2. Role of $N^{+}R_3$ polar group:
- Allows interactions with moisture
- Promotes a surfactant function

How does the quaternary ammonium silane exhibit anti-soiling and anti-static properties?

1 The non polar hydrophobic tail of the Si-QUAT reduces surface energy. Hydrophobicity is enhanced due to its co-condensed structure with the OPSZ primer. Water droplets roll off from the surface carrying away soiling more easily.

2 The long aliphatic chain of the Si-QUAT promotes lubricity (water sliding angles are reduced). At the same time the $N^{+}R_3$ polar group allows strong interactions with moisture, thus increasing conductivity of the coating's surface (without affecting the hydrophobic properties of the coating). As a result its tendency to accumulate static electricity is dramatically reduced.

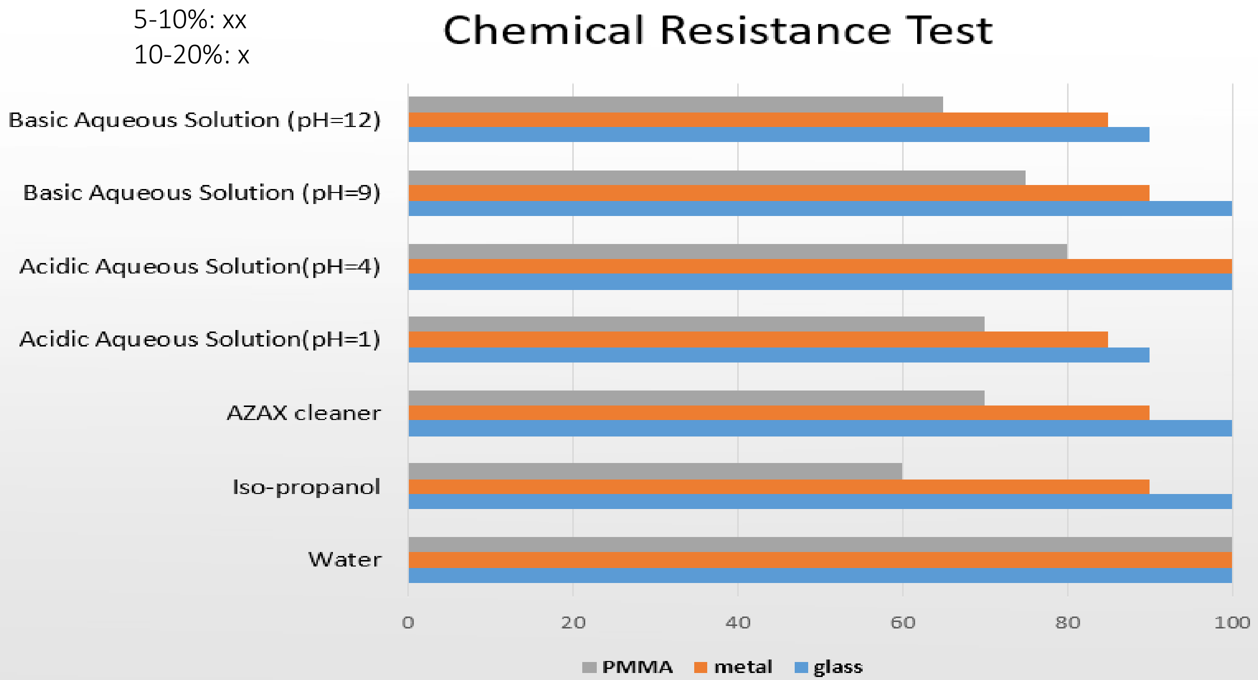
Chemical Resistance Test

Chemical Resistance test carried out by immersing glass, metal and PMMA substrates to various chemicals for 7 days; comparison by WCA before and after the immersion

	Water	AZAX Cleaner	Iso-propanol	pH=1	pH=4	pH=9	pH=12
Glass	XXX	XXX	XXX	XX	XXX	XXX	XX
Metal	XXX	XXX	XX	XX	XXX	XXX	XX
Plastic	XXX	XXX			X	XX	

xxx: excellent x: slightly resistant
xx: good -: not resistant

WCA dergadation:
<5%: xxx
5-10%: xx
10-20%: x



✓ *The coating exhibits high chemical resistance probably due to strong crosslinking reactions between the primer and the top coat*.

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CONCLUSIONS

Conclusions

- A <u>facile</u> preparation mode for the production of durable and transparent anti-soiling and antistatic coatings based on siloxane/polysilazane nanostructures has been hereby presented. This comprises an OPSZ primer acting as a polymeric binder with both the substrate and the top coat and a quaternary ammonium silane acting as an anti-soiling agent. The two layers are applied sequentially via the sol-gel method.

- The coating presents improved <u>anti-static</u> and <u>anti-soiling</u> attributes due to the multifunctional role of the Si-QUAT, as well as to the interconnected network of highly crosslinked nanostructures between the OPSZ and the Si-QUAT which positively affects adhesion, hardness, uniformity and smoothness.

  - The primer promotes <u>adherence</u> of the coating to <u>non-hydroxylated</u> substrates.

  - The coating has <u>high abrasion</u> and <u>chemical resistance</u> without affecting the substrate’s optical properties.

  - Facility in <u>industrial</u> implementation-large substrates made of various materials can be easily coated.

<u>Acknowledgement</u>

This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code:T1EDK-04949).

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