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Superhydrophobic Coatings to Prevent Corrosion in Electronics

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Abstract: The corrosion of electronics is a sweeping problem. Corrosion of electronics even at a small scale can render them unproductive. It happens due to the contact between metal surfaces and oxidizing agents, superhydrophobic coatings promise to address just that. They have predominant water phobic character. This review article describes how corrosion affects electronics followed by the introduction of superhydrophobicity and its theory about the Young's equation, the Wenzel equation, and the Cassie-Baxter model. Superhydrophobicity and its presence in nature is concisely discussed in the introduction. It further reviews the various ways by which superhydrophobic coatings can be produced and their effect on corrosion. Finally the challenges this coating faces and importance of these coatings is discussed upon in conclusion.
Keywords: Corrosion, Electronics, Superhydrophobic Coatings, Nature, Water phobic.

I. INTRODUCTION

Electronic machineries are very prone to getting corroded due to harsh environments present. Corrosion is the degradation of metal over a period of time due to its chemical reaction with its surrounding environmental contaminants. This corrosion of electronic machinery and resulting huge losses has always been big challenge. [1] [2] [3] With time the electronic devices have become smaller and thereby making them vulnerable to corrosion in even milder environments. The tolerance of microchips used in various electronic devices against it is very less and therefore can lead to their failures. Corrosion mechanism has been a subject of ample research. Failure of electronic machines due to corrosion is becoming an alarming issue. [2]
Humidity has been a gigantic issue and a most common one whenever it comes to degradation of electronics over a period of time. Atmosphere containing particular gases such as Sulphur in sever and wastewater plants, chemical and petroleum plants can trigger consequential corrosion for metals put to use in electrical apparatus [2].

Table 1: Effects of varying humidity levels *[IEC 60068-1, table I]*.

Humidity	Principal Effects	Typical failure
High relative humidity	Moisture absorption or adsorption Swelling Loss of mechanical strength Corrosion and electrolysis Increased conductivity of insulators Increase of dielectric constant ϵ_r	Physical breakdown, insulation failure, mechanical failure, increase of dielectric losses
Low relative humidity	Desiccation Embrittlement Loss of mechanical strength Shrinkage Abrasion of moving contacts	Mechanical failure, cracking

Breakdown of electronic devices may occur due to interruption in electrical contact between relays or connectors because of humidity conditions. A demolishing situation would be when water will stay on surfaces or in gaps because then even a well-sheltered surface can corrode.
However a technology, which takes a cue from nature, can protect surfaces from getting corroded. This technology is biomimetic superhydrophobic coating. Superhydrobhic coating as the name suggests highly repels water. It has non wetting characteristic. When a drop of water falls on a superhydrophic coating containing surface, it bounces off [4][5]. Superhydrophobicity is observed in

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nature on the leaves of the Lotus flower, also on the wings of some insects [6]. It also furnishes the surface with self- cleansing property [7] [8]. If the contact angle of water drop on a solid surface is more than 150 degrees then the surface is called superhydrophic. The water or an oil droplet may roll off from the surface. As there will be no contact of moisture with electronic systems, there will be no oxidation and hence no corrosion. For the manufacturing of superhydrophobic surfaces low surface energy and a rough surface topology is required. The theory of superhydrophic surfaces will be covered in this review.

Figure 1 - Water repellency observed on leaf surface

Furthermore, distinct properties such as flexibility, breathability, color change, anisotropy, reversibility, electrowetting and transparency are also subsumed into biomimetic superhydrophobic surfaces [8]. This review paper will discuss the recent advancements in various new technologies and methods that have been invented to apply superhydrophobic coating, the chemistry behind it and its functions. Lastly this review will give conclusion on this technology.

II. THEORY

Lotus leaf is a popular example for understanding superhydrophobic surfaces. The water contact angle is a parameter to check hydrophobicity of a surface. It is the angle between the interfaces of solid-liquid, liquid-air and solid-air. If this angle is > 90 then the surface is deemed as hydrophobic, and if it is > 150 degrees then it is said to be superhydrophobic. The water droplets that fall on lotus leaves do not get absorbed or stay but roll off from the surface taking with them all the dirt and contaminants thus also causing a cleansing effect.
The factors found to be responsible for this kind of behaviour are a concoction of

A. Low interfacial energy of the surface,
B. Roughness of the surface.

The low interfacial energy present is due to waxy deposits on the surface [4].There are many other examples too for superhydrophobic surfaces in nature (cicada's wing, rose petals and mosquito compound eyes).
Therefore, altering the surface chemistry of substrates would be a way to make them superhydrophobic. There are three equations that give an idea about the wettability of surface under different conditions - The Young's equation, the Wenzel equation, and the Cassie-Baxter model.
Young's equation elucidates the wettability of a uniform surface by the equation:

$$\sigma sv = \sigma sl + \sigma lv * \cos\theta$$

where
1) σsv represents surface free energy of solid
2) σsl denotes the surface energy between the solid and liquid an
3) σlv expresses surface free energy between liquid- vapor interface.

However Young's equation is based on the assumption of a perfectly smooth and homogenous surface. Surfaces in nature contain much roughness and defects. To deal with this Wenzel established a roughness factor (r) in the equation. This roughness factor is greater than or equal to 1:
The Wenzel equation where θw = contact angle of a rough surface:

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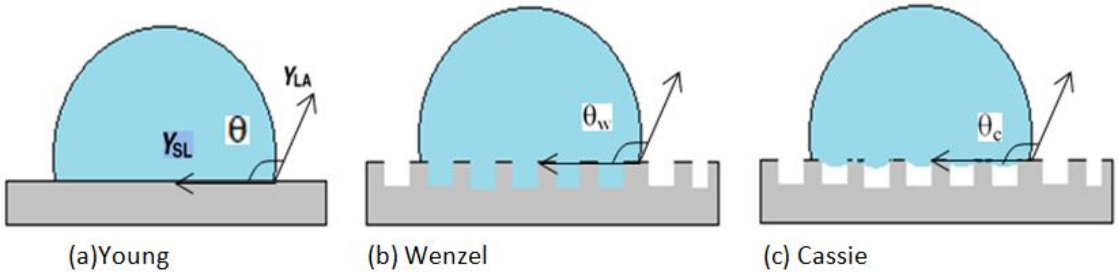
$$\cos \theta_w = r \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} = r\cos\theta$$

Figure 2: Different models of wettability.



The third model is the Cassie- Baxter model which assumes that the liquid does not penetrate into the outgrowths on the surface rather is suspended on them. The Cassie-Baxter equation-

$\cos \theta_{cw} = f\, r * \cos\theta + f - 1$

Where f is fraction of solid surface which is wetted, r is the roughness factor, θcw is the contact angle.

III.FORMATION OF SUPERHYDROPHOBIC COATING

The combination of less surface energy and roughness of surface both is required to create a superhydrophobic surface. Silicon, Steel, Aluminium, Copper are some of the metals widely used in electronics. They can be, either, treated to induce roughness and then coated with a low surface energy material or a substrate having low surface energy can be modified to be rough to produce a superhydrophobic surface.

Superhydrophobic coatings for metals:

Silicon resin and fluorine resin have low surface energies (~22mN/m and ~10mN/m respectively) but to be superhydrophobic they need to be provided with roughness to be able to increase the water contact angle >150°.

There are various ways to increase the surface roughness of metals to impart superhydrophobicity when coated with low surface energy coatings. Some of them are Etching, sol-gel method, hydrothermal method and nano-composite coating.

A. Nano-Titanium Dioxide Coatings

Minerals such as TiO_2 and ZnO can also be used to make superhydrophobic coatings [10][11] . Nano- Titanium dioxide superhydrophobic coating on stainless steel shows a very good corrosion resistance. A sol-gel solution of TiO2 along with ultra-fine particles is prepared and deposited on stainless steel. A nano-TiO2 coating is formed on it. Ethyl acetoacetate (EAcAc) is used as a chelating agent titanium dioxide in this process. A hydrothermal treatment is further done to optimize the properties of surface. A prefabricated fluoroalkylsilane (FAS) is then applied to increase the hydrophobic property for the surface of the coating. [10]

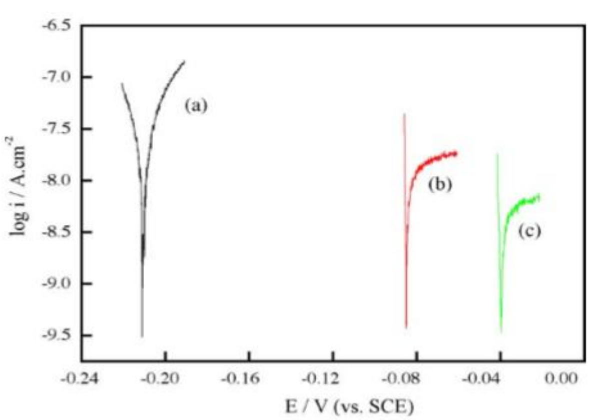


Fig. 3. (a) Polarization curves for bare stainless steel and films in oxygen-saturated Ringer solution. (a)Bare steel; (b)TiO2/ stainless steel coatings;(c) FAS/TiO2/stainless steel coatings [11]

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The nano TiO_2/ FAS coated stainless steel show less current densities than uncoated steel. The hydrophobic coatings are reported to show excellent corrosion resistance in Ringer solution.

B. Hydrothermal Method

This is an important method to create surface roughness on alloys. It is created under raised heat and pressure conditions in aqueous surroundings. This is an environmental friendly method since the chemical in use is only H_2O or dilute H_2O_2. The corrosion tolerance of metals is further increased due to emergence of hydroxide and oxide protective layers. Treatment with Perchlorooctlytrichlorosilane is second step to obtain superhydrophobic surfaces. The perchlorooctlytrichlorosilane lowers surface energy thereby making the surface superhydrophobic.[11]

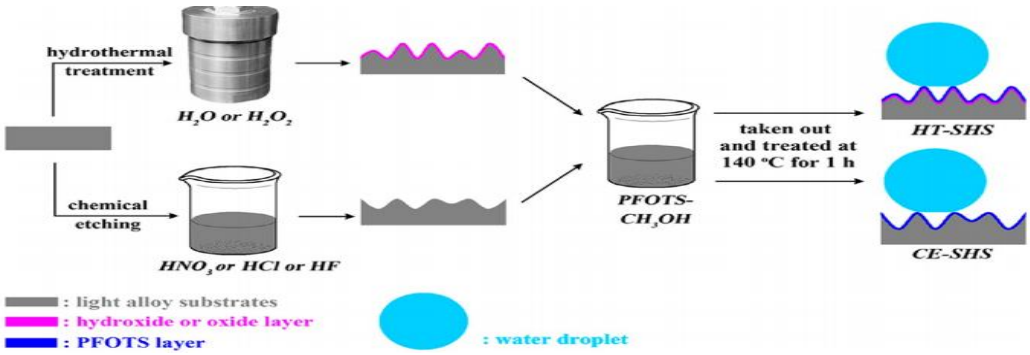

Fig. 4. Superhydrophobic surface preparation by hydrothermal method or chemical etching. [11]

Ou et. Al reported improved corrosion resistance in Mg, Al and Ti alloys upon their hydrothermal treatment and chemical modification with -perfluorooctyltriethoxysilane (PFOTES). Tafel plots obtained after exposure to NaCl were obtained that indicated lower I_{corr} value denoting lower corrosion dynamic rate and positive E_{corr} representing lower corrosion thermodynamical tendency.

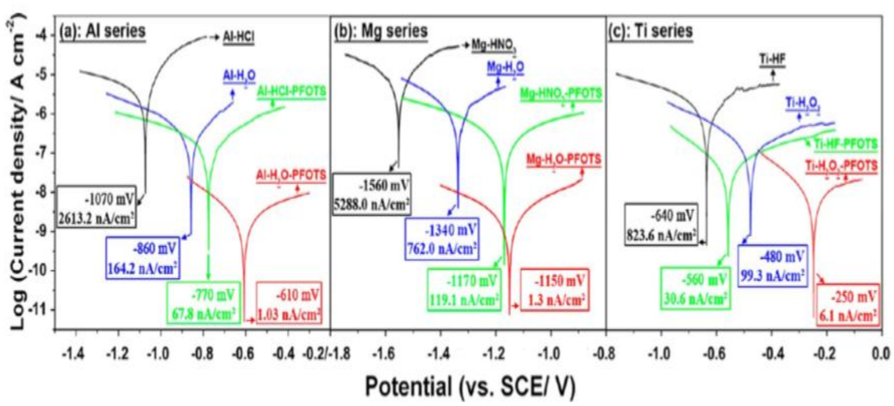

Fig.5. Tafel plots of various samples. [11]

C. Etching

Chemical etching of the imperfections and impurities on the surface and further grafting them by low surface energy materials is done to obtain superhydrophobicity. [12-13] Microstructures are formed on the surface which lead to an increase in contact angle. The microstructures here are more tolerant to external forces as compared to wet chemical reactions since they are etched out from bulk materials.[14] It is one of the cheapest and easiest process. However, the etching process involves usage of harsh chemicals and is therefore harmful for health of workers and the environment. Chemical, laser and plasma etching are some of the methods which are recently used. [15][16][17]

A superhydrophobic aluminium was fabricated by chemical etching in NaClO, followed by passivation by hexadecyltrimethoxysilane. The superhydrophobic sample showed lower corrosion current density when dipped in 3.5% NaCl solution for a period of 7 days as compared to hydrophobic and hydrophilic samples. [18]

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D. Sol- gel

High temperature or high pressure is not obligatory for this process. It can be applied on a range of substrates. [19, 20] A silica coating that was superhydrophobic in nature was made by dip coating copper substrate in a sol–gel solution. The sol-gel solution had methanol, ammonia, methyltriethoxysilane and water. [20]

The coating created showcased a roll-off angle lower than 7 degrees and water contact angle of 155 degrees. The superhydrophobicity was conserved after dipping in 50 weight percentage hydrochloric acid for 100 hours.

The various other methods to produce superhydrophobicity on the surface include anodization [21] , spray coating [22] , layer by layer assembly [23] , electrodeposition [24] , templating [25] etc

IV. CONCLUSIONS

A good boost to the research in Superhydrophobic coatings has been given since the1990's .These coatings enhance corrosion resistance and can be applied upon many substrates. The mechanism behind superhydrophobic coating is well understood and therefore much more avenues for its application can be found out. However these coating still face a number of issues for their large scale deployment to prevent corrosion in electronics. They are found to hinder transparency- this can be a problem where it is a necessary requirement. The roughness responsible for superhydrophobic behaviour can be affected due to external forces, thus affecting its property. Superhydrophobic coatings also face problems at high temperature as they can melt away. Nevertheless, these coatings also provide properties such as self- cleansing, anti- fouling and anti- icing along with prevention of corrosion which make them worthy to be researched upon.

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