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Kh. M. E. Hashem^a; N. A. Ramadan^b

^a Chemistry Dept., Faculty of Science, Ain-Shams University, Cairo ^b Egyptian Petroleum Research-Institute, Nasr City, Cairo, Egypt

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Communication

ANTI-CORROSION COATINGS PRODUCED FROM ORGANOSILICON COMPOUNDS

Kh. M. E. HASHEM

Chemistry Dept., Faculty of Science, Ain-Shams University, Cairo

and

N. A. RAMADAN

Egyptian Petroleum Research-Institute, Nasr City, Cairo, Egypt

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A series of tetra-alkoxy, tetra-phenoxy and tri-alkylaryl silanes compounds were prepared neatly to be tested as corrosion inhibitors for carbon-steel alloys. Following the standard procedure, specimens from the carbon-steel alloy were prepared and divided into pairs. The surface of each pair was thinly coated with one of the above organosilicon compounds. From each pair; a specimen was thermally treated at a temperature of 750°C for ten minutes, while the other was left at ambient temperature for 3 days. The physical properties such as; electrical conductivity, surface morphology, composition, structure and degree of coherence of each residual film were measured and investigated by using; digital potentiometer, SEM, EDS, X-ray diffraction and SEM edged cross-section micrograph respectively. From the outcoming data it was noticed that, the specimens coated with tetra-phenoxy silane produced (at the two extreme temperatures) needle shaped silicon dioxide films which varied in their physical properties. However, it is believed that the optimum properties could be achieved by adjusting the temperature and thermal treatment time ranges individually. Although, the occurrence percentage of silicon metal in the tetra-alkoxy silane series were higher than that in the tetra-phenoxy silane, discrete and very thin silicon dioxide films were formed. This could be attributed to the low volatile silica and boiling points of tetra-alkoxy silane.

INTRODUCTION

Carbon steel is widely used in chemical process plants such as high pressure and temperature boiler's tubes of electrical power stations. However, it is relatively low corrosion resistant either on water-side or fire-side because both of them are exposed to scale forming-ions such as Ca^{2+} , Mg^{2+} , OH^- , SO_4^{2-} and low melting vanadates. The main role of the deposited scale is lowering heat transfer through the steel tubes and forming various localized corrosion types.

Several protected programs are currently used to combat corrosion and scaling in steel heat exchangers.^{1–3} One of these programs is based on using organosilicon compounds to form stable protective coatings on the surface of metals at high temperatures. The mechanism of protection is based on the interaction of two processes; Metal in form of organosilicon compounds coatings was brought into contact with the surface of carbon steel, and this was followed by gradual diffusion of silicon into the lattice of carbon steel at different temperatures. Alkyle-silicate coatings cure through absorption of atmospheric moisture and harden more rapidly at higher temperatures, while the water based silicates cure through moisture removal and will not cure properly in a moist atmosphere.⁴

The performance of silicate esters, as temporary protectives on steel was studied in the liquid phase at atmospheric pressure.⁵ The inhibition role of these organo-silicon compounds over mild steel was investigated by the first rust spot appearance method. The increase of weight of test specimens, owing to corrosion at various testing times, was investigated. Also, it has been found that the corrosion inhibition properties of silicate esters (tetra-alkoxysilanes) increase due to high molecular weight branched ester isomers.⁶

In the present study, the capability of some organosilicon compounds to produce stable coatings at two extreme temperatures on carbon steel A192 specimens' surfaces was investigated.

RESULTS AND DISCUSSION

Table I shows the visual inspection of the coatings produced by tetra-alkoxy-, tetraphenoxy- and tri-alkylaryl silanes on carbon steel at the two extreme temperatures. Generally, the delamination phenomenon is the final structure for the produced coatings either at ambient or high temperature.

At ambient temperature (25°C), compounds F and G exhibited shortly quick surface changes within 210 and 25 minutes, respectively. The changes were terminated by forming an insulating, flaky, brown and thin coatings, which were easily peeled by nails. These evidences could be attributed to fast hydrolysis rate for F and G compounds.¹¹ However, the variation in the specifications of the coatings produced by the other compounds supported the action of atmospheric moisture on the hydrolysis rates.⁴ In spite of the decreasing of the Si percent in the tetra-alkoxy silanes series (A–F), it was noticed that the insulation properties proportionally increased with the molecular weight. Although the silicon percentages in tri-alkylaryl silanes (H, I) were in the same order like tetra-alkoxy silane (A), the corresponding coatings completely varied in their degrees of coherence and colour properties. These phenomena could be attributed to the role of intramolecular oxygen-silicon bonds. At high temperature (750°C) the properties of the formed coatings were nearly similar to their correspondings at low temperature (25°C). The variations could be attributed to the time of pyrolysis.

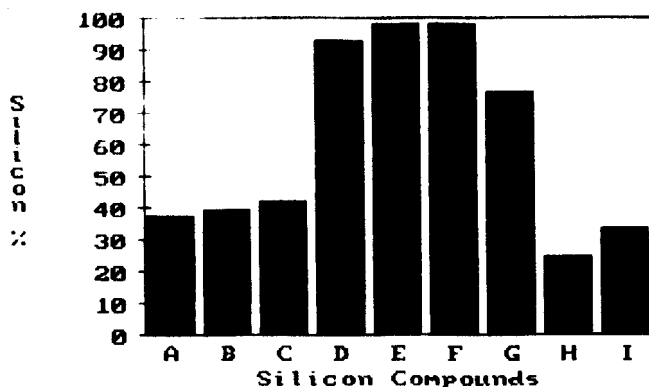
Fig. 1 shows the histogrammic representation for the residual silicon in organo-silicon coatings on carbon steel (A192), which was determined by EDS technique. Fig. 1a–b represents the percentage of silicon in each coating produced at ambient temperature for 3 days and at 750°C for 10 minutes respectively. Using EDS technique, analysis of the coatings on the specimens' surfaces proved that silicon and iron were only detectable metals in normalized percentages. Thus, it could be concluded that:

1. The concentration of the detectable iron by EDS is the net of the diffused and allowable substrate iron.
2. The concentration of the residual silicon in coatings is inversely proportional with the penetration power of the incident X-ray.
3. The structure of coatings enriched with residual silicon characterized with high porosity, low permeability and low coherence with the carbon steel surface.
4. The composition of coatings either produced at ambient or high temperature mainly consist of low or high synthesized silicon dioxide (SiO₂).

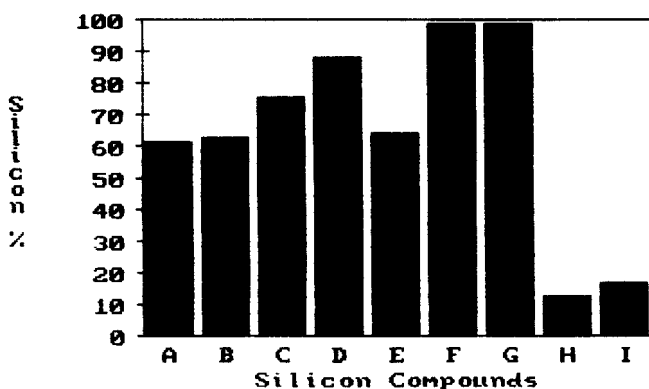
TABLE I
The visual inspection and the physical properties of the coatings on carbon-steel produced from organosilicon compounds

Organosilicon compounds			Silicon Coatings by Hydrolysis			Silicon coatings by pyrolysis		
Ref.	Formula	Si%	Hydrolysis at Ambient Temperature for 3 Days			Pyrolysis at 750 °C for 10 minutes		
			Colour	Insulation	Coherence	Colour	Insulation	Coherence
A	(C ₂ H ₅ O) ₄ Si	13.462	distinct white & brown spots for- med after 55 hrs	low insulation	brittle & weak co- herence film.	dark brown layer	low insulation	low coherence remo- ved by nails.
B	(n-C ₃ H ₇ O) ₄ Si	10.606	brown layer for- med after 62 hrs	low insulation	weak coherence film.	dark brown layer	low insulation	low coherence remo- ved by nails.
C	(n-C ₄ H ₉ O) ₄ Si	8.75	light brown one layer formed after 42 hrs.	low insulation	thick layer easily removed by nails.	dark brown layer	partially low insulation	low coherence remo- ved by nails.
D	(n-C ₆ H ₁₃ O) ₄ Si	7.447	brown layer for- med after 17 hrs	high insulation	flaky layer easily removed by nails.	dark brown layer	partially low insulation	low coherence remo- ved by nails.
E	(n-C ₆ H ₁₃ O) ₄ Si	6.481	brown layer for- med after 28 hrs	high insulation	flaky layer easily removed by nails.	dark brown layer	low coherence remo- ved by nails.	
F	(C ₆ H ₁₃ O) ₄ Si	6.604	dark brown form- ed within 210min	high insulation	flaky layer easily removed by nails.	outer brown & inner colourless layers.	high insulation	duplex layer * phenomena
G	(ph-O) ₄ Si	7.0	dark brown spon- taneously formed after 25 mins.	high insulation	brittle flaky lay- er easily removed by nails.			
H	m-Me-ph-Si-Me ₃	17.073	greyish green formed after 35 hours.	low insulation	strong coherence with substrate rem- oved by scratching	greyish green layer	partially low insulation	strong coherence with less cavity structure.
I	p-Me-ph-Si-Me ₃	17.073	greyish green formed after 42 hours.	low insulation	strong coherence with substrate rem- oved by scratching			

* Duplex layer phenomena, the outer layer could be removed by nails, while the inner has been removed by hard scratching.



a) The percentages of the silicon on coatings produced at ambient temperature (25°C) for 3 days.



b) The percentages of silicon on coatings produced at 750°C for 10 minutes.

FIGURE 1 Histogramic representation for the residual silicon in organosilicon coatings on carbon steel (A192) determined by EDS technique.

The appearance of delamination phenomena with the coatings produced from tetra-alkoxy silanes compounds (A–G), accompanied by coherence failure with the carbon steel surface, could be, attributed to low gaseous permeabilities of coatings. In further detail the creepage of the trapped oxygen, and/or carbon-dioxide (produced as a result of the hydrolysis and the pyrolysis of organosilicon compounds, between metal and coating interfaces were in their minimum rates, due to low gaseous permeability of the protected coating. In spite of decreasing the concentration of the residual silicon, in the coatings produced from tri-alkylaryl silanes (H, I), their coherence with the metal surface was found relatively stronger than those exhibited by tetra-alkoxy-(A–F) and tetra-phenoxy-(G) silanes. The reason could be explained by absence of intramolecular oxygen.

Fig. 1b indicates that the increase in concentration of residual silicon, in the protective organosilicon coatings, concurs with pyrolysis rather than the hydrolysis process. This phenomenon drew attention to the comprehensive role of some

Collected List for the Most Probably Identified Compounds

Symbol	Name	Formula	Specific d's values			Ref.
			1	2	3	
A	-----	Fe ₂ SiO ₄	2.83	2.52	1.78	20-1139
B	Cristobolite	SiO ₂	4.05	2.49	2.84	11-695
	low-syn.					
C	Cristobolite	SiO ₂	4.11	2.52	1.64	27-605
	high-syn.					
D	Tridymite	SiO ₂	4.27	4.08	3.80	14-260
	syn.					

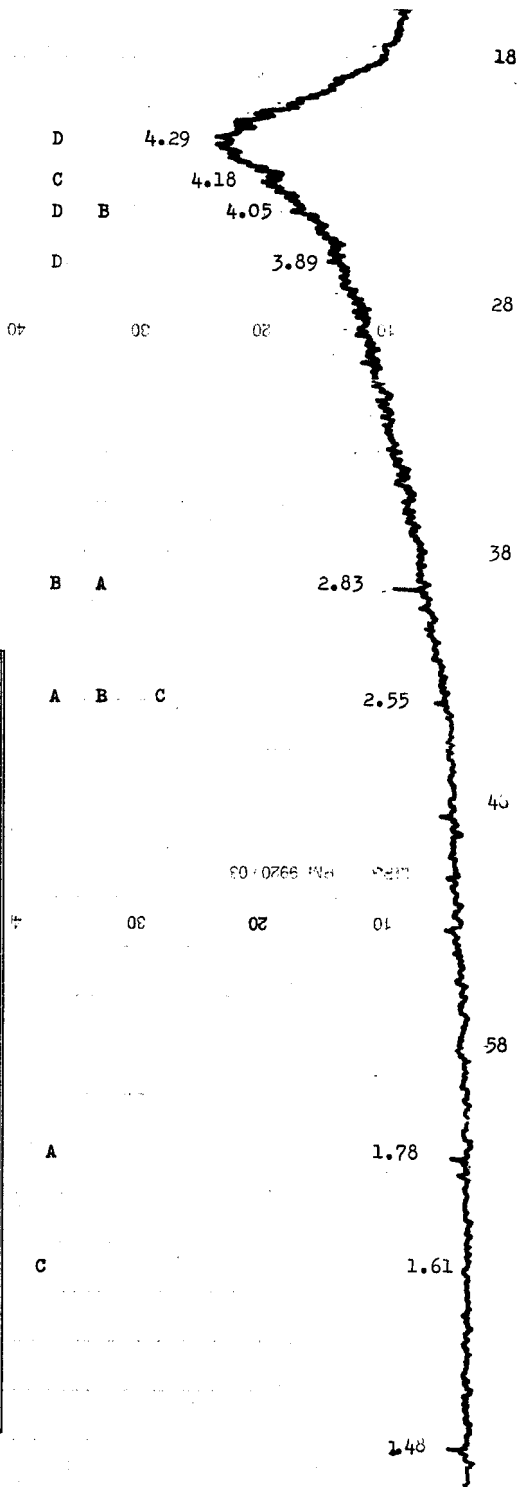


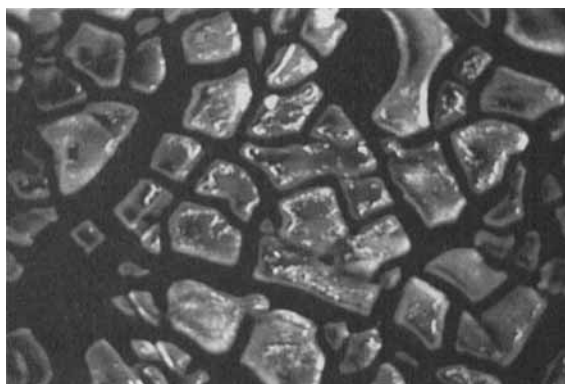
FIGURE 2 Typical X-ray diffraction complex pattern for a mixed sample including the organosilicon compounds' coatings.

practical parameters e.g., temperature, concentration and pyrolysis time, on improving the physical properties of the protective silicon coatings.

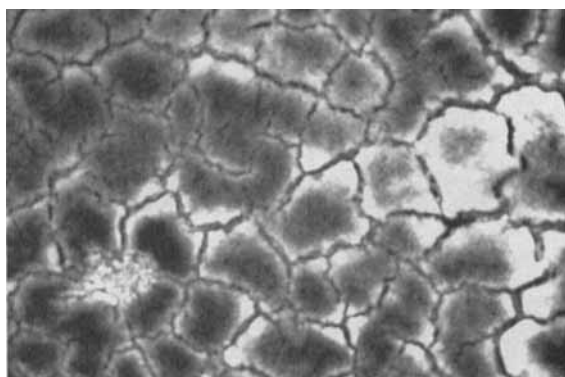
Fig. 2 represents the X-ray diffraction complex pattern, for a mixed sample including the coatings produced from the used organosilicon compounds (A–I),



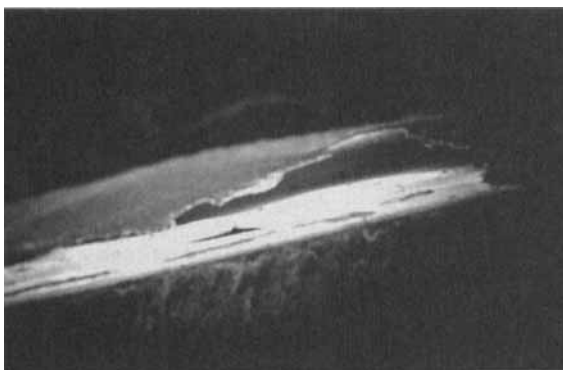
a) Typical porous surface texture and morphology for the formed coatings at 250x.



b) Amorphism phenomenon for the formed coatings crystals at 1500x.



c) Cross-edged micrograph to clear the thickness of the formed coatings in respect to the substrate 150x.



d) Magnification for one ripple at 2000x to clear the degree of coherence.



e) Magnification of one ripple at 2000x to clear the duplex layer phenomenon.

FIGURE 3 The SEM micrographs for some characteristic phenomena for silicon coatings.

at ambient and high temperature. Fig. 2, also includes a collected list of the most probably identified compounds with their characteristic three d's values. From the data given in Fig. 2, the following remarks could be drawn:

1. Fe_2SiO_4 is designated as low intensity lines. This observation indicates that this product would reflect an idea about the rate of corrosion for carbon steel and/or the partition coefficient of migrated iron through the silicon coatings.
2. SiO_2 is identified in three phases called cristobolite low-syn., cristobolite high-syn. and tridymite synthesis. The characteristic lines for the three detectable phases are weak intensities due to amorphism of synthesized crystals.

Fig. 3 shows the SEM micrographs which were exposed at different locations and magnifications for some characteristic phenomena for silicon coatings.

Fig. 3(a) is a typical high porous texture for the silicon coatings produced either during hydrolysis or pyrolysis of the organosilicon compounds. This micrograph was exposed at 250x to support the low gaseous permeability concept.

Fig. 3(b) was exposed at 1500x to make the idea behind amorphism phenomenon clear.

Fig. 3(c) is a cross edged micrograph which was exposed at 150x, to show the thickness of the formed coating in respect to the substrate. The ripple marks are the characteristic structures for the formed coatings. To determine the degree of coherence, only one ripple has been magnified to 2000x (see Fig. 3d). The interface cavity between coating and substrate support the intramolecular trapped oxygen concepts. On the other hand Fig. 3(e) and (f) show the duplex layers' phenomena, in which, the inner layer is coherent with the metal surface. Also, it is colourless and thinner than the outer layer.

The above findings lead to conclude that the work is still in progress, willing to reach the optimum conditions at which strong and coherent protective silicon coatings on carbon steel (A192) could be achieved.

EXPERIMENTAL

1) *Preparation of the organosilicon compounds:* a) Tetra-ethoxy,⁷ tetra-propoxy,⁷ tetra-butoxy,⁷ tetra-pentoxy,⁷ tetra-hexyloxy⁸ and tetra-cyclohexyloxy silicanes,⁸ were prepared through the reaction of proper alcohols with SiCl_4 . b) Tetra-phenoxy silane was prepared through the reaction of phenol with SiCl_4 .⁹ c) Trimethyl-m-tolyl and trimethyl-p-tolyl silanes were prepared through the reaction of the proper Grignard aromatic derivatives with Me_3SiCl .¹⁰

2. *Preparation of carbon steel specimens with coatings:* Specimens were cut from unused carbon-steel A192 tube as regular edged cuboids with dimensions $2.2 \times 0.6 \times 0.3$ cm. Each specimen was cleaned, polished with 600 and 400 grade emery paper, rinsed with water, degreased with acetone, weighed and finally stored under vacuum after wrapping it with adhesive thin paper.

The specimens were divided into pairs. Each pair was coated with one of the synthesized compounds. One from each pair was then thermally treated at 750°C for 10 minutes under the atmospheric pressure, while the other was left at ambient temperature of 25°C for 3 days.

3) *Techniques of Analysis:* The visual inspection and electrical conductivity test were carried out to investigate the inversed relation between the applied temperatures and their times on the physical properties of the organosilicon coatings such as: colour, electrical resistance and double layer properties.

The degree of coherence of each coating was relatively determined by applying the ultrasonic vibrational technique using an ultrasonic cleaner model Astrason 7E, since the stability of the coating on carbon steel was in direct proportionality with the time at which the first portion of coating was removed.

SEM model JEOL-JSM-T2000 linked with simultaneous multi-element analyzer 860/500 dual disc Energy Dispersive System (EDS), was used to study the morphologies and structures of the created organosilicon coatings at two extreme temperatures. The morphological micrographs were exposed by a camera model JEOL-T20-CSI at magnification depending on the purpose of investigation. EDS spectra was analyzed to evaluate the relative concentration of the deposited silicon on the specimens' surfaces.

To identify the new phases of silicon which have been formed after thermal treatment. X-ray diffractometer Philips 1976 model 1390 was used to produce a diffraction pattern for each coating. The patterns were analyzed by applying Fink's procedure with using the most-three d's values

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