

## FORMATION OF PROTECTIVE NANO-LAYERS ON STEEL SURFACE FROM GAS-VAPOR PHASE

**<sup>1</sup>V.I. Vorobyova PhD in Technical Sciences, assistant, <sup>1</sup>O.E. Chygyrynets' Doctor in Technical Sciences, professor, <sup>1</sup>Y.F. Fatyeyev PhD in Chemistry, docent, <sup>1</sup>Pylypenko T.M. PhD in Technical Sciences, docent, <sup>1</sup>Overchenko T.A., senior Lecturer**

<sup>1</sup>*Department of Physical Chemistry, National Technical University of Ukraine "Kiev Polytechnic Institute".  
Ave Peremogy, 37, Kiev-03056, Ukraine.*

<sup>2</sup>*Ukrainian State University of Chemical Technology, Dnipro, Ukraine  
ave. Gagarina, 8, m. Dnipropetrovsk, 49005  
E-mail: viktorkathebest@yandex.ru*

**Abstract:** *The results of obtained information will help to deepen scientific principles for the development of volatile corrosion inhibitors. Their inhibition action was evaluated on corrosion of mild steel under a thin-film electrolyte consisting of simulated water using the weight loss method installed a synergistic increase in the inhibitory activity of a plant extract when administered alkoxy-silanes. compounds. The obtained results improve the scientific basis for selection the synergistic components in plant extracts.*

**Анотація:** *Прискореними гравіметричним методом корозійних випробувань в умовах періодичної конденсації вологи встановлено синергетичне підвищення інгібуючої ефективності рослинного екстракту при введенні алкоксисиланів. Отримані результати поглиблюють наукові основи підбору синергетичних компонентів до рослинних екстрактів.*

Mild steel is the most common form of steel and because of its low cost it is chief material of construction. Mild steel have good strength, hard and can be bent, worked or can be welded into an endless variety of shapes for uses from vehicles (like cars and ships) to building materials. Because of its unique properties like, very cheap, high strength, hardness and easy availability, it has wide range of applications in nut bolt, chains, hinges, knives, pipes, magnets, military equipment etc. Metal and their alloys are exposed to aggressive environment under atmospheric condition during the manufacture, processing, storage, or transportation and can accelerate the degradation of the metal, alloys and their products. In such cases, the corrosion prevention methods like water-displacing products (oil or grease), water-absorption products (silica gel) and dehumidification are not significant due to high labor, material cost for the application and removal of product and difficulty to calculate specific moisture.

Corrosion is a fundamental process playing an important role in economics and safety, particularly for metals and alloys. Steel is widely used in a broad spectrum of industries and machinery, however; it tends to be corroded. The corrosion of steel is a fundamental academic and industrial concern that has been received a considerable amount of attention. Atmospheric corrosion of metals in closed spaces, such as in parcels, and during storage and shipment, can be temporarily prevented by the use of certain substances called vapour space corrosion inhibitors (VPCI). A vapour phase corrosion inhibitor (VPI) is a compound that has the ability to vaporize and condense on a metallic surface to make it less susceptible to corrosion. The main advantage of VPIs compared with conventional corrosion control methods stems from their gas-phase transport. A VPI reaches the metallic surfaces without contacting the surface directly. The efficacy, convenience, and cost effectiveness of VPIs made their application for rust control almost universal in automotive-manufacturing, steel-making, ship-building, power generation, and defence production. It was found that certain specific VPI formulations can in fact be toxic. Synthetic organic inhibitors are widely used to protect metals against corrosion.

Most of the volatile corrosion inhibitors are synthetic chemicals, expensive, and very hazardous to environments. Thus, alternative of environmental-friendly VPIs is under consideration. The extract of oilcake rape seeds (*Brassicaceae*), which contains many chemicals

compounds, may be used as VCIs [1-5]. The authors found that the isopropanol extract of rapeseed meal provides an effective level of corrosion protection at the level of 70%. It was known that synergistic inhibition effect (synergism) is a combined action of compounds greater in total effect than the sum of the individual effects. It was known that synergistic inhibition effect (synergism) is a combined action of compounds greater in total effect than the sum of the individual effects. In the last two decades, the potential of organofunctional silane molecules for the replacement of chrome conversion treatments has been the topic of a huge number of studies. Silanes have been widely studied as coupling agents between inorganic and organic materials since. Concerning corrosion science, a lot of efforts have been made to apply these materials as adhesion promoters between metallic substrates and organic coatings used for protection against corrosion phenomena. The chemistry of silanes and the mechanism of interaction of these molecules with a metallic substrate and an organic coating have been widely explained. Taking into consideration that (3-aminopropyl) triethoxysilane is a volatile compound with equilibrium vapor pressure  $p_s = 1,5 \times 10^{-6}$  mm Hg at 25°C and contains an amino group that confers its main properties, then, in combination with the aforementioned, its positive action on the protective properties of VCIs could be expected.

The purpose of the present work is to investigate synergist inhibitory activity the extract of oilcake rape seeds and volatile alkoxysilanes.

### **Experimental**

**Materials and apparatus.** The corrosion test was carried out using mild steel strips. The composition of the mild steel (%): C 60.15; Mn 0.20–0.45; P 60.03; S 60.035 and Al, P 0.02. First, the strips were polished by emery paper of 1/0, 2/0 and 3/0 then rinsed with twice-distilled water, degreased and dried at room temperature. Extracts of the rapeseed cake was prepared by macerating in the 2-propanol alcohol for 48 hours and filtered through filter paper.

Weight loss measurements were made by specimens of mild steel having dimensions of 2.5 cm x 2.0 cm x 0.025 cm, and a hole was drilled in each for suspending the samples. The samples were grinded with SiC paper to 1000 mesh and were then cleaned in alcohol and rinsed before drying at room temperature. The final geometrical area was 25 cm<sup>2</sup>. The gravimetric measurement was conducted by suspending the samples in a 250 cm<sup>3</sup> conical flask with a tight-fitting rubber cork containing a small dish. The VCIs were dispersed in the dish. The samples with freshly prepared surface were mounted on the flask with and without 1.0 g inhibitor, respectively. After inhibitor film-forming period of 3 days, 15 cm<sup>3</sup> deionized water was added. The test process included cyclic warming and cooling of the samples in a corrosion testing chamber of varying humidity. One cycle included an 8 h exposure in the thermostat (50 ± 1°C), and 16 h exposure at room temperature. This set up was kept for 14 days. The mill scale on the specimen was removed by using a suitable pickling solution, i.e., Clarke's solution (a mixture containing concentrated hydrochloric acid, 2% antimony trioxide (Sb<sub>2</sub>O<sub>3</sub>) and 5% stannous chloride (SnCl<sub>2</sub>), washed, dried, and then weighed. All the experiments were performed in duplicate and average values are reported.

The surface morphology and coating were examined by SEM XL 30.

### **Results and discussion.**

The results show that the combined adsorption film extract of grape pomace and volatile alkoxysilanes is a good inhibitor (99,0 %.). However, combined use of a plant extract, volatile alkoxysilanes promotes a greater increase inhibitory protection, indicating probably the formation of a dense structure film on the metal surface. The corrosion rate and inhibition effectiveness for the extract of of oilcake rape seeds film-forming specimens were 0,1879 g m<sup>-2</sup> h<sup>-1</sup> and 70,6%, respectively.

One of such ways can involve the after effect of VCI (i.e., its ability to protect steel on by a protective film even after the inhibitor has been removed from the corrosive medium). The after effect can be provided by both relatively thick ("phase") which often form when metal is kept in the vapour phase containing a VCI. This effect is based on the irreversible inhibitor adsorption, which depends on the chemical structure of the inhibitor.

We studied the after effects of films obtained on still samples by immersing them in the vapour phase containing this inhibitor.

Table 1

**Calculated corrosion rates ( $\text{g m}^{-2} \text{h}^{-1}$ ) and inhibition efficiency (%) for volatile corrosion inhibition test**

Samples	Corrosion rate / $\text{g m}^{-2} \text{h}^{-1}$	IE/%
Control	0,1879	-
Extract of grape pomace	0,0552	70,60
Extract of grape pomace and (3-aminopropyl) triethoxysilane	0,0019	99,0

The resulting film have been sufficiently stable and completely protected the steel in the vapour phase of 3 % NaCl and 1 N  $\text{Na}_2\text{SO}_4$  for 5-days and 10 days, respectively (Table 2). The inhibition efficiency of the steel samples treated extract of hop cones were 50,5 and 57,3 % for the 3 % NaCl and 1 N  $\text{Na}_2\text{SO}_4$  respectively.

The inhibition efficiency of the steel samples treated composition inhibitor were 71,0 and 80,3 for the 3 % NaCl and 1 N  $\text{Na}_2\text{SO}_4$  respectively.

Hence, metal protection requires that they are always present in the corrosive medium, and can provide metal protection due to the post-treatment effect, inhibition efficiency by irreversibly adsorbed molecules.

Table 2

**Aftereffect of VCI on mild steel in the vapour phase (Test duration 504 h, time  $\tau$  of the film formation, 120 h)**

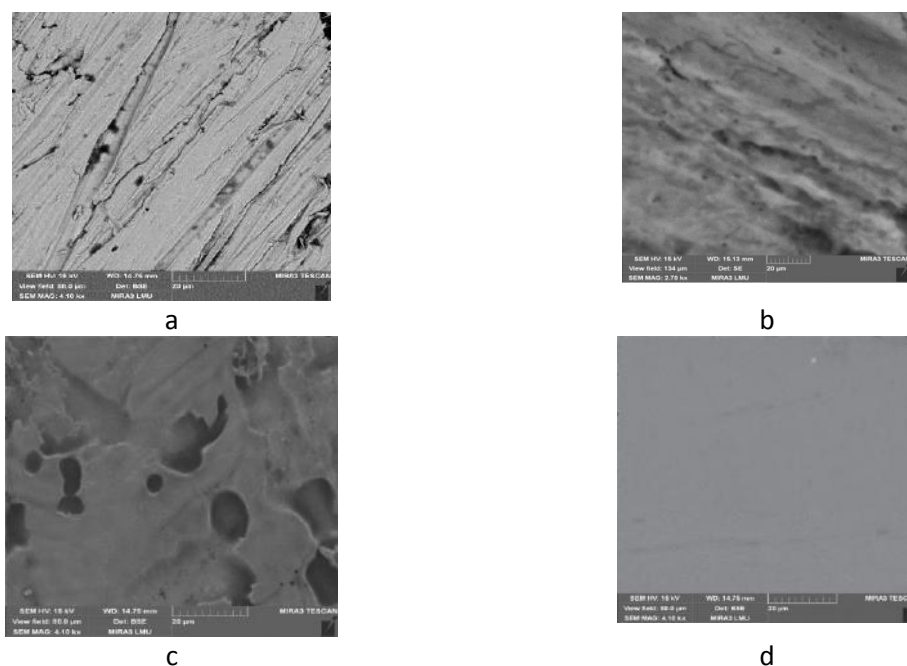
Test conditions	Volatile corrosion inhibitor	IE/%
Sample in the vapour phase of 3 % NaCl	Extract of grape pomace	50,5
	Extract of grape pomace and (3-aminopropyl) triethoxysilane	71,0
Sample in the vapour phase of 1 N $\text{Na}_2\text{SO}_4$	Extract of grape pomace	57,3
	Extract of grape pomace and (3-aminopropyl) triethoxysilane	80,3

The adsorption process due to the action of volatile compounds of rapeseed cake extract and volatile alkoxy silanes was monitored with an SEM. SEM images are shown in Fig. 1. The surface morphology of the sample before exposure to grape pomace extract indicates there were a few scratches from the mechanical polishing treatment. The following images (Fig. 1 b) are of the steel surface after 48 h of exposure for the film-forming of volatile compounds of grape pomace, respectively. It shows a thin and covering surface film composed of many particles. Investigation by Stratmann [8] suggested that adsorption of VCI may form a few protective monolayers. These particles may be mainly composed of the adsorbed of of grape pomace molecule.

The volatile chemical composition the extract of cake oil rape seeds is highly complex containing glycosides, nucleosides, ketone, aldehyde, saturated and unsaturated fatty acids, sterols and alkaloids. The most abundant compounds were Oleic, Linoleic and Palmitic acid (about 62%).

The synergistic inhibition effects of the extract of grape pomace and alkoxy silanes on the corrosion of mild steel was studied by weight loss, potentiodynamic polarization curves, FT-IR methods. In the presence of water, the hydrolyzable alkoxy group tends to form a reactive silanol group (SiOH), which reacts with a hydroxyl group on the metal surface to form siloxane (Si-O-Si) and metasiloxane (Me-O-Si) covalent bonds. The hydrolysis reaction proceeds spontaneously, without catalysts, but acids which are adsorbed on the steel surface from the vapor phase a plant extract accelerate the hydrolysis of silanes. As a result of the hydrolysis of alkoxy groups, (3-aminopropyl) triethoxysilane is transformed into silanol, the molecules of which interact with each other and form siloxane bonds. Because the coupling agents are trifunctional with regard to the alkoxy group, then, as a result of condensation, their molecules can form branched and interlaced polyorganosiloxane structures. This ability of silanes to undergo hydrolysis and further

transformations during interactions with water vapors seemed to be very attractive for the purposeful development of a nanosized protective coating on metal surfaces from the gas–vapor phase.



*Fig. 1 SEM images of the carbon steel surface: (a) initial surface; after 48 h exposure for film-forming extract of grape pomace (b), mixture extract of grape pomace and (3-aminopropyl) triethoxysilane; after 96 h exposure for film-forming mixture extract of grape pomace and (3-aminopropyl) triethoxysilane*

## CONCLUSIONS

A novel volatile corrosion inhibitor (VCI), composition extract of oilcake rape seeds and (3-aminopropyl) triethoxysilane, was developed for temporary protection of carbon steel and the maximum inhibition efficiency is about 99,0%.

## REFERENCES

1. Vorob'iova V.I. Mechanism of Formation of the Protective Films on Steel by Volatile Compounds of Rapeseed Cake / V.I. Vorob'iova, O.E. Chygyrynets, O.I. Vasylykevych // *Materials Science* .- 2015, Vol. 50, Is. 5, Pp 726-735.
2. Chygyrynets' O.E. A study of rapeseed cake extract as eco-friendly vapor phase corrosion inhibitor / O.E. Chygyrynets', V.I. Vorobyova // *Chemistry and Chemical Technology* .- 2014. Vol. 8, – №. 2. – С. 235–242.
3. Vorobyova V.I. Synergistic inhibition effects the extract of oilcake rape seeds /major components and triethylamine on the corrosion of steel / V міжнародна наукова конференція матеріали для роботи в екстремальних умовах – 5 // V.I. Vorobyova, O.E. Chygyrynets, S.Yu. Lipatov // 03 – 05 грудня 2015 р. С. 157-159.
4. Vorobyova V.I. Volatile corrosion inhibitor film formation on carbon steel surface / V.I. Vorobyova, O.E. Chygyrynets', M.I. Vorobyova // *HighMatTech: 4-th Intern. conf.*, October 7-11, 2013: Proceedings of the conference. – Kiev: 2013. – P. 331.