

ANNOTATION

Explanatory note to the master's thesis Kotliarenko A. on “Combinational inhibitor of atmospheric corrosion of steel based on grape pomace extract” – Igor Sikorsky Kyiv Polytechnic Institute, 2017. 128 p., 14 fig., 33 tables, 109 sources.

Object of research – the inhibition of the atmospheric corrosion of steel volatile corrosion inhibitors.

Subject of research – corrosion performance combinational inhibitor based on grape pomace extract.

Purpose - to evaluate the efficiency of anticorrosive action and formation mechanism of a protective film of grape extract and combinational inhibitor based on it as volatile corrosion inhibitors of steel.

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 phase corrosion inhibitors. Volatile corrosion inhibitors (VCI) have been used for years to temporarily protect metals from corrosion in extreme conditions. The VCIs are known to have extended corrosion inhibiting properties to a metal surface due to their volatilization within an enclosed space. Most of the volatile corrosion inhibitors are synthetic chemicals, expensive, and very hazardous to environments. That's why application of natural products as anticorrosion agents is of interest to research. Natural products are known to be incredibly rich sources of naturally synthesized chemicals for most applications. Plant extracts are bio-degradable, non-toxic and of potentially low cost. Most of the naturally occurring substances are safe and can be extracted by simple procedures. Thus, an alternative of environmental-friendly VPIs is under consideration promising raw materials for the development of VPIs, we can mention organic substances of vegetable origin because, as a rule, natural raw materials contain a large number of biologically active substances and the process of extraction is, as a rule, more cost-efficient than chemical synthesis.

As one of the simplest, convenient for applications, and efficient methods of the corrosion protection of the metal products under the conditions of atmospheric corrosion (AC), we can mention the application of volatile inhibitors. At present, volatile

atmospheric corrosion inhibitors (VACI) occupy a special place among the inhibitors of atmospheric corrosion because they can protect products of complex shapes made of both ferrous and nonferrous metals.

As VACI, several thousands of compounds of various chemical classes have been investigated and recommended but most of them do not meet the contemporary ecological and economic requirements. Moreover, new requirements are imposed on the methods of their manufacturing. The organization of the process of multistage synthesis is a complex and high-cost process. This is why the VACI whose preparation, in the ideal case, is reduced to simple mixing of the components prove to be most promising. Hence, it is important to develop volatile inhibitors of atmospheric corrosion characterized not only by high efficiency and environmental safety but also by a simple procedure of preparation.

As promising raw materials for the development of VACI, we can mention organic substances of vegetable origin because, as a rule, natural raw materials contain a large number of biologically active substances and the process of extraction is, as a rule, more cost-efficient than chemical synthesis.

It was shown that the wastes of the production of wine from grapes can be a source of natural organic compounds for the preparation of VACI. Despite the wide complex of bioactive substances can hardly find any application. In most cases, it is simply burned or disposed in one or another way. For this reason, we study the chemical composition of volatile fractions of isopropanol grapes extract and its inhibiting efficiency.

It is possible to improve the protective action of VCIs, i.e., isopropanol extract of grape and (3-amino propyl)triethoxysilane and polydimethylsiloxane, via their joint application, which facilitates the formation of nanosized films of inhibitor on the surface of metals.

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. 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 and are reported. Silanes films not only ensure the adhesion between metal substrates and organic coatings but they also provide a thin, but efficient, barrier against oxygen diffusion to the metal interface. Compared to the traditional chromate conversion treatments the only drawback of silanes is that they do not provide an active protection to the metallic substrate. In fact, when water and aggressive ions reach the surface of the metal, silane layers are not able to ensure an active inhibition of the corrosion process as well as chromates compounds.

Because organosilanes hydrolyze before reacting with each other or with the hydroxyl groups present at a substrate surface, it is important to understand the reaction kinetics. The hydrolysis reaction can be catalyzed using either an acid or a base. Mechanisms of acid- and base catalyzed hydrolysis of organosilanes have been extensively studied since their discovery.

Acid catalyzed hydrolysis involves the protonation of the leaving OR group followed by a bimolecular S_N2 -type displacement of the leaving group by water.

Base catalyzed hydrolysis involves attack on silicon by a hydroxyl ion to form a pentacoordinate intermediate followed by bimolecular displacement of alkoxy by hydroxyl. Any high-electron acceptors group next to the Si atom will dramatically increase hydrolysis under basic pH.

The rate of hydrolysis by both mechanisms is influenced by the nature of the organic group on silicon as well as the leaving alkoxy group. Another factor is pH. As pH changes, so does the hydrolysis rate. This is true for both acid- and base-catalyzed reactions.

As soon as alkoxy groups begin hydrolyzing, condensation to highmolecular-weight species may occur. The rates of both hydrolysis and condensation are influenced by changing pH levels. This is true whether the reaction is catalyzed by acid or base. However, the optimum pH for hydrolysis is not optimum for condensation. Finding the best balance between hydrolysis and condensation is one of the keys to the successful utilization of organosilane chemistry for a specific application.

As a result of the hydrolysis of alkoxylic groups, (3aminopropyl)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 cocondensation, 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.

Materials and Methods. Anticorrosion efficiency of the extract of grape was studied. For the extraction of chemically active substances from vegetable raw materials, we used isopropyl alcohol. The extract was prepared by holding preliminarily ground vegetable raw materials in isopropyl alcohol at a ratio of 1 g of grapes waste per 10 ml of the solvent for 24 h. We obtained a light-brown liquid with a smell of isopropyl alcohol.

The composition of volatile substances of the extract was studied by the method of chromatography-and-mass spectrometry by using a FINIGAN FOCUS gas chromatograph with an HP-5MS capillary column 30 m in length and 0.25 mm in diameter under the following conditions: temperature of injector + 250°C; temperature of detector + 280°C; thickness of the phase 0.25 µm; helium as a carrier gas; flow of the carrier gas 1.5 mliter/min; the temperature conditions of chromatographic analysis (program) were as follows: an initial temperature of the column of 100°C and a heating rate of the column (temperature gradient) of 10°C/min up to 280°C; the mass range was 30–500 a.m.u.; the sample was introduced with a split flow of 15 mliter/min; the volume of the sample was 2 µl.

The components were identified by comparing the peak retention times in the chromatogram and the complete mass-spectra of individual components with the corresponding results for pure compounds in the NIST-5 Mass Spectral Library.

The relative contents of the chemical components of the extract were found by the method of internal normalization of the areas of peaks without correcting the sensitivity coefficients.

The anticorrosion efficiency of the extract was evaluated by the method of accelerated tests under the condition of moisture condensation in the solution and natural experimental. According to the first technique, samples of St3 steel were placed in a hermetically sealed vessel with distilled water or another more aggressive environmental (3% NaCl and 1% NaNO₃) and a tank with the volatile inhibitor in a heat chamber, in which a mode of periodic moisture condensation (a test cycle at 40°C for 8 h and at 25°C for 16 h) was maintained. The total test time was 21 days.

According to the second technique, the VACI was used in the composition of inhibited paper. For this purpose, we impregnated craft paper with the inhibitor, wrapped samples by it and then by a polyethylene cover, and held them under room conditions for 3 days to form a protective film. The testing conditions were identical to the natural atmospheric testing conditions by six months. Prior to investigation, samples 50 × 20 × 1 mm in sizes were cleaned with emery paper of different grit, degreased, and held in an atmosphere of vapor of inhibitors for three days. We assessed visually the efficiency of corrosion protection and calculated the negative mass index of the corrosion rate K_m – and degree of protection Z . The change in the mass of samples was found by weighing. Corrosion products were removed by etching in an inhibited 10% HCl solution for 1 min.

The adsorption dynamics of the protective film of volatile substances on the surface for 2 days was assessed according to the changes in the electrochemical behavior of the metal held in vapors of the volatile compounds of the extract. As a model electrolyte for atmospheric corrosion, we used 1 N Na₂SO₄. For the polarization electrochemical investigations, an installation consisting of a PI-50-1 potentiostat, a PR-8 programmer, and a MM-5 mixer was used. An St3 sample with an area of 0.385 cm₂ pressed into teflon served as a working electrode, a sulfurprotoxide electrode served as a reference electrode, and a platinum electrode was used as an auxiliary electrode. The values of potentials were converted to the normal hydrogen scale. Prior to taking polarization curves, we treated the electrode with emery paper of different grit, degreased with acetone, and held for 24–72 h in a tightly closed tank with a volume of 100 ml over a weighing bottle with 2 ml of the grape extract.

The surface morphology and coating were examined by FEI E-SEM XL 30. For SEM images, 1cm² specimen sample were taken.

The registration of IR - spectra the extract of plant material was performed on IR - Fourier - spectrometer Jasco FT/IR – 4000. To characterize adsorbed film on the metal, 1 cm² surface area of mild steel was exposed to both gas mediums for certain hours and used for surface analysis by FT/IR spectrum. The registration of IR - reflectance spectrums of the sample surface pretreated volatile corrosion inhibitors was performed by IR Fourier-transformed spectroscopy (Perkin Elmer) in the range of – 4000 - 630cm⁻¹.

Quantum chemical calculations have been performed by the HyperChem 7 package. The geometry optimization was obtained by application of the restricted Hartree-Fock method (RHF) using MNDO approach with PM3 parameterization. According to Koopman's theorem, the frontier orbital energies EHOMO and ELUMO are related to the ionization potential I, and the electron affinity A of iron and the inhibitor molecule by the following relations: $A = -ELUMO$, $I = -EHOMO$.

The softness σ of the inhibitor molecule is simply the inverse of the hardness: $\sigma = 1/\eta$. If bulk iron metal and the inhibitor molecule are brought together, the flow of electrons will occur from the molecule of lower electronegativity to the iron that has higher electronegativity until the value of the chemical potential becomes equal.

Quantum chemical calculations has been found to be successful in providing insight into chemical reactivity and selectivity in terms of global molecular properties, such as electronegativity (χ) and chemical potential (μ). Thus, for an N-electron system with total electronic energy (E) and an external potential $v(r)$; the chemical potential (μ), which is also the negative of the electronegativity (χ), has been defined as the first derivative of the E with respect to N at constant $v(r)$. (3)

It has been reported that the more stable molecular structure has the largest HOMO-LUMO energy gap. Therefore, an electronic system with a larger HOMO-LUMO gap should be less reactive than one having a smaller gap. This relationship is based on the Maximum Hardness Principle, which states that 'there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible'. This principle is among the most widely accepted electronic principles of chemical reactivity and a formal proof of

this principle was given by Parr and Chattaraj. If bulk iron metal and the inhibitor molecule are brought together, the flow of electrons will occur from the molecule of lower electronegativity to the iron that has higher electronegativity until the value of the chemical potential becomes equal. The fraction of electrons transferred from the inhibitor molecule to the iron atom will then be given. The global electrophilicity index (ω) was introduced by Parr et al..

The electronegativity of metal surface is replaced by the work function for Fe surface, theoretically equals 4.82 eV and the hardness, metal metal which equals 0eV for bulk metals.

Results and Discussion. By the chromatography-and-mass spectrometry method, in the volatile fraction of the isopropanol extract of the grape, we detected 21 compounds. Among these, we can mention aliphatic and aromatic aldehydes, saturated and unsaturated fatty acids. Among the aldehydes in the larger number, the saturated and unsaturated aldehydes were identified: Caproaldehyde (9.1%), Heptanaldehyde (8.7%), Phenylacetaldehyde (6.5%), Butanal (5.8%), Nonanaldehyde (5.0%), Citral (2.3%).

Most of these substances are known as corrosion inhibitors in various media and often as main components of the compositions.

The analysis of the results of accelerated corrosion tests shows that the volatile fractions of the extract protect steel from corrosion under the conditions of periodic moisture condensation when the extract is used both from the vapor phase and in the form of inhibited paper with degrees of protection of about 99 and 95%, respectively.

It should be noted that the treatment of specimens in the vapor phase of individual isopropanol does not improve the corrosion resistance of the metal.

We recorded the formation of the first signs of corrosion on the metal surface on the fifth day in the absence of treatment. At the same time, these signs appeared only after 10-day holding in the case of treatment by the volatile fractions of the grape extract from the vapor phase and after 15-day holding in the case of wrapping in the inhibited paper. It is worth noting that the efficiency of volatile substances of the extract also depends on the volume ratio of the inhibiting component in the closed space or in the carrier, i.e., in the inhibited paper.

The electrochemical behavior of steel was investigated in 1 N Na₂SO₄ after the formation of the protective film for 24,48,72 h for different contents of inhibitor in the closed volume.

Since the film is formed from the gas-vapor phase for a certain period of time, we studied the influence of the time of holding of a specimen of St3 steel in the vapor phase of the extract on the kinetics of electrode reactions. As a result of treatment of the metal by the volatile fractions of the extract, the currentless potential shifts to the positive side even after holding for 24 h.

As the time of treatment of the metal by the volatile compounds of the extract increases to 48 h, the increase in the inhibiting efficiency becomes especially pronounced, which corresponds to the saturation of the surface with the inhibitor and the formation of the strongest bonds between the inhibitor and the metal. The diffusion currents differ insignificantly, which shows that the influence of the inhibitor on the rate of the cathodic reaction of oxygen reduction is negligible. With further increase in the holding time to 72 h, the anticorrosion efficiency somewhat decreases. This is probably connected with the competing character of adsorption of different components of the extractive part, which leads to the desorption of some compounds from the surface.

As an important characteristic of the films formed on the metal surfaces in the vapor of the volatile inhibitor, we can mention their ability to preserve protective properties (aftereffect) in the course of time in the absence of VACI in corrosive media.

For this reason, we investigated the aftereffect of films formed on the metal surface after preliminary holding of the specimens in the vapor of the isopropanol extract of the grape waste. It was shown that these films give the required aftereffect under the conditions of periodic condensation of moisture over 3% NaCl and 1% NaNO₃ aqueous solutions.

SEM analyses were conducted in order to characterize the protective layer that formed on the low carbon steel surface. SEM images initial surface and after 48 h for VCI film-forming are shown. The surface morphology of the sample before exposure to volatiles of extract indicates there were a few scratches from the mechanical polishing treatment. This image displays a freshly polished steel surface. The following is of the

steel surface after 48 h of exposure for the film-forming of the rape-cake extract. It shows a thin and covering surface film.

The electronic parameters calculated include: E (HOMO), E (LUMO), energy gap etc,. The calculated results show that all the molecules have high propensity as electron donors, have low energy gap and electronegativity (high reactivity), are good nucleophiles characterized by low values of global electrophilicity index.

The results of obtained information will help to deepen scientific principles for the development of volatile corrosion inhibitors. The volatiles of inhibitor mixtures based on isopropanol extract of grape were analyzed by GC–MS. The content additionally introduced silanes and siloxane compounds. Their inhibition action was evaluated on corrosion of mild steel under a thinfilm electrolyte consisting of simulated water using the weight loss and electrochemical polarization resistance method installed a synergistic increase in the inhibitory activity of a plant extract when administered silanes and siloxane compounds. The obtained results improve the scientific basis for selection the synergistic components in plant extracts.

It is shown that the main components of the gas–vapor part of the isopropanol extract of grape are aliphatic and aromatic aldehydes, saturated and unsaturated fat acids. The results of accelerated tests performed under conditions of humid atmosphere and polarization investigations in the model electrolyte enable us to conclude that the analyzed extract guarantees high levels of anticorrosion protection of the metal in the case of its application both from the vapor phase and on the carrier (inhibiting paper). The corrosion rate of steel decreases as the concentration of the inhibitor increases. The formation of a film with maximum protective characteristics is completed after holding of St3 steel for 48 h in the vapor of volatile compounds of the extract. It is characterized by the aftereffect under the conditions of periodic condensation of moisture

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