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Investigation of the Efficiency of Inhibitors of Atmospheric Corrosion

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The aim of researches was an estimation of efficiency of the worked out volatile corrosion inhibitors on the basis of plant materials. It is established that the high level of anticorrosive defense is achieved by using them as an inhibitive paper and during application from a steam phase. Electrochemical polarization methods of research in modeling environments showed that the developed compositions exceed the protective properties of the known inhibitor of the NDA when using in a slightly aggressive industrial and marine atmosphere.

Keywords: VOLATILE INHIBITOR, PLANT MATERIAL, ATMOSPHERIC CORROSION, INHIBITIVE PAPER, ELECTROCHEMICAL METHOD

Introduction

Continuous development of the industry, especially in themetallurgical production, makes it necessary to delivery products to consumers without the corrosive lesions. Transportation and long-term storage, marine and rail transportation of metal products are inconceivable without the use of corrosion protection, because evenslight corrosion damage can disable devices and equipment, which cost commensurate with the cost of the metal itself.

Traditional methods of protection include changes in the composition of alloys or application to the metal coatings. However, in some cases, such as protection devices and electrical and electronic equipment, complex machinery and equipment, consisting of a variety of metals, alloys, semiconductors and non-metallic materials, the use of classical methods of corrosion control is economically inefficient, and often not possible. In this case, the most modern and reliable method is the use of volatile corrosion inhibitors (VCI), which do not require the artificial application or removal from metal surfaces.

Under the conditions of atmospheric corrosion preservation is usually limited to the introduction of a source of VCI to the package with metal, and degreasing - the removal of packaging material. Their use is almost always justified when there is a possibility at least for partially hermetic sealing of the protected space. VCI is an effective means of temporary protection against corrosion, aging and biodegradation of complex steel structures, products and technology for the period of storage, transportation or interoperational protection. In an inhomogeneous medium (the liquid-gas) VCI protect metal in the whole volume, including the phase boundary, where the corrosion process is often most intense. VCI are applicable in all industries, all manufacturing processes and at all stages of the existence and operation of the product.

In addition, when used correctly VCI reduces the final cost of production by increasing the service life of products to simplify and reduce the time of repair, to simplify the process due to the exclusion of the standard operations such as degreasing and cleaning, rust removal, etching, sandblasting, etc.

The formation of a protective film of VCI is due to the transfer of the active ingredient of the media (film, paper) or from space, its saturated vapor to the surface of metal products. Evaporating at ambient temperature, such inhibitors in the form of vapors reach the metal and adsorbing on the surface, provide protection for the product. Vapours of VCI easily penetrate into the cracks and gaps that are not available for contact inhibitors, and deceleration corrosion processes provide inhibition of a layer of corrosion products and deposits [1]. It is important to note that volatile inhibitors are a self-regulating system, i.e. with increasing aggressiveness of the environment (especially temperature), the evaporation rate of VCI increases, which subsequent ensures the effective protection of metal products.

The composition of volatile inhibitors includes compounds containing groups that can influence the kinetics of electrode reactions causing corrosion process and groups, giving the substance of the necessary volatility. Therefore, VCI are basically a reaction product of a weak base (amines and their derivatives) and the weak organic and inorganic acids: nitrites, chromates, benzoates, nitrophenols, as well as azoles, heteroalkylated amines, phosphorus-containing compounds and other substances [1].

The most widely used compositional compounds VCI are those including nitrogen-containing compounds, azoles, and phenolic compounds. These inhibitors provide effective protection of metal products made of ferrous and nonferrous metals through the use of components with different physical and chemical characteristics. VCI are used in their natural form, in the form of solutions, aerosols, as well as on special media - silica, alumina, poroplast and other organic and inorganic materials, as well as inhibited paper in conjunction with the waterproof barrier packaging materials or in the form of polymer inhibited films.

It should be noted that a significant part of VCI in the past produced currently do not meet modern environmental standards [2]. For this reason, for example, the use of nitrogen-containing inhibitors is sharply limited. Besides, most of the components used in obtaining VCI, are rather scarce, expensive and often toxic.

The new requirements apply to the production methods of VCI. Organization of multi-step synthesis in the current conditions is a complicated and expensive task. The most promising of VCI, which it is possible to obtain by one or two-reactor scheme, and ideally is reduced to mixing of components. However, one should note that in Ukraine there is no domestic production of VCI. Lack of VCI and materials based on them is filled with imported goods prohibitively expensive and not always of high quality.

Nowadays an American corporation "Cortec" is the recognized world leader in the design and manufacture of anti-corrosion and materials containing VCI, and has subsidiaries and representative offices in many European countries, including Russia.

The company offers a wide range of products that allows the temporary protection of products during the manufacturing process at the plant (VCI (V_PCI) 408, 415, 419, 345, 316, etc.), protection during shipment and storage, as well as long-lasting protection at conservation equipment (inhibited paper and packaging "Cortec". polyethylene film VPCI-126, emitters).

Not less large and well-known manufacturer of VCI and materials based on them is a U.S. firm Northern Technologies Intern., which has organized a production under the brand name ZIRAST not only in the USA but also in many European countries. In Russia, a manufacturer and supplier of inhibited materials ZIRAST since 1999 is the JSC "MostNIK" (Moscow). More than 25 years of experience in the application in 48 countries shows the high efficiency of various means of protection against corrosion, produced by this firm [3].

Currently inhibited film of company ZIRAST is used for protection rolled steel at major industrial enterprises, such as JSC "VAZ", JSC "GAZ", OJSC "UAZ", JSC "Severstal", JSC "Lipetsk Metallurgical Works", etc. It should be noted that none of the Ukrainian metallurgical plants apply volatile inhibitors.

Similar products VCI materials to the consumer is represented by Japanese firms «Nitto» and «Aicello chemical». These are tapes (57 GO / c) and polyethylene films (E-MASK RB-S Series), containing a volatile inhibitor of the company «Nitto» and polyethylene film company «Aicello chemical». Tape (57 GO / c) is intended for the mechanical and corrosion protection of different kinds of objects of irregular shape, embedded into the ground or water.

JSC "VNIINeftehim" (Russia) mastered the production technology of industrial volatile corrosion inhibitors of ВНХ group, allowing to protect ferrous and nonferrous metals (ВНХ-Л-49, ВНХ-Л-20). [4]. On the basis of a volatile inhibitor ВНХ-Л-49 LLC "Gammasintez" (Russia) offers inhibited polyethylene film "Gamma".

The Institute of Physical Chemistry and Electrochemistry of RAS designed and organized production of volatile nitrogen-containing inhibitors a series of technological ИФХАН (ИФХАН 1, 8, 61, 100, 118) for the protection of ferrous and nonferrous metals from atmospheric corrosion. VCI ИФХАН can be used for conservation of energy equipment, pipes, tanks, cooling systems and air conditioning products of complex configuration, precision engineering, metal powders, metal ceramics, microelectronics, etc.

In Ukraine there were attempts to implement a laboratory synthesis of a number of substances that have been proposed as a volatile series nitrogen-containing inhibitors ЛКС, however wide dissemination they had not received [5]. Therefore, the problem of creating new, efficient, responsible environmental and economic requirements of the VCI based on domestic raw materials is very acute.

One of the promising directions in the development of corrosion-resistant materials is the use of plant products with high efficiency actions. From the analysis of scientific and technical literature there is known to inhibit the positive experience of using the properties of plant materials and by-products of agricultural production not only in Ukraine but also abroad [6].

The plant raw materials contain a set of such compounds as aliphatic aldehydes and fatty acid derivatives of phenol, guaiacol, sulfur compounds, which are often used in anti-corrosion compositions [7].

Thus, the plant raw material contains a wide range of organic compounds potentially capable of inhibiting corrosion processes on metal, so they are increasingly used in the creation of new anti-corrosion materials. In Ukraine thousands of tons of plant crops are processed every year, and thus a large amount of waste that may be an alternative raw material for the creation of inhibiting compositions.

The authors established [8] that the volatile compounds of plant origin can be used to create compositions for inhibiting the protection against atmospheric corrosion of metals. Given the amount of raw materials and anticorrosive performance, it was determined that types of plant materials promising for the creation of inhibiting compositions are hops, traditionally grown in large quantities in the Ukraine, rapeseed meal, a byproduct of processing oilseed rape to produce biodiesel.

It is shown experimentally that the volatile fraction of vegetable raw materials provide stable protection of the metal in the initial period of the possible development of corrosion. But it often requires a more prolonged and effective protective action of VCI. Therefore, the authors developed the composition of volatile inhibitors with plant organic compounds [9], possessing a long anti-corrosion properties.

As noted earlier, VCI may be applied contactly from the air saturated vapor of inhibitor or by using the media in a variety of packaging materials such as inhibited paper, silica gel, inhibited polymeric film. However, data on the protective ability of volatile nitrogen-containing inhibitors designed based on the method of application and storage of processed metals are absent.

Therefore, the aim of this study was to evaluate the effectiveness of volatile corrosion inhibitors designed at the application of traditional methods and in different weather conditions.

Methodology

We studied the anticorrosion efficiency of the developed on the basis of plant material compositions of volatile inhibitors ЛВГ-1, ЛВГ-2. For obtaining ЛВГ-1 "aromatic" hops variety was used, and for ЛВГ-2 - rapeseed meal. For comparative evaluation was investigated the famous volatile dicyclohexylamine nitrite corrosion inhibitor (НДА).

The application of volatile inhibitors film was carried out according to three methods. In accordance with the first one the inhibitor was applied by dipping the samples contact metal directly into the solution of the investigated VCI. In the second method inhibitors were applied by exposing the metal in their vapors in a closed container for three days. On the third method investigated VCI were applied within the inhibited paper. The introduction of the inhibitor in a paper was made by impregnating it. The samples were packed into inhibited paper and then placed in a plastic bag and kept for 3 days at room conditions.

Accelerated corrosion testing was carried out in a sealed desiccator, on the bottom of which there was distilled water. In the first and second method at the bottom of the desiccator, except water, put an additional beaker with an inhibitor. To accelerate the corrosion processes on all methods of the samples were immersed in a desiccator and placed in a heat chamber, which supported the mode of periodic condensation (1 cycle for 8 h at 40 ° C and 16 h at 25 ° C). Duration of test method 1 was 20 days, by the method 2 - 45 days, by the method 3 - 60 days. Since the НДА is not a known inhibitor of the contact, its trials were conducted only by the second and third method.

Prior to testing samples of Ст3 (size 50x20x1 mm) were cleaned with sandpaper of different grits, degreased, were kept in an atmosphere of vapors of inhibitors for 3 days. The change in mass of samples was estimated by gravimetric method. Corrosion products were removed by etching in a 1% solution of inhibited hydrochloric acid. Evaluation of the effectiveness of corrosion protection is done visually, as well as by a negative indicator of the corrosion rate of the mass - K_m, the degree of protection Z, inhibition coefficient γ [10].

Comparative evaluation of resistance of Ст3 samples in the protection of volatile inhibitors in a variety of atmospheric conditions is made by their electrochemical behavior in model media. As an electrolyte, simulating the conditions of slightly aggressive atmosphere, were used 1 Na2SO4, industrial atmosphere, filled with man-made emissions of gases (SO_2, SO_3, CO_2 etc.) - slightly acidic (pH 2) solution of distilled water, marine atmosphere - 3% NaCl solution.

Electrochemical studies were performed in an apparatus for polarization measurements, including a potentiostat ПИ-50-1, П-8 programmer and mixer MM-5. The working electrode was used steel Ст3 sample area 0.385 $см^2$, pressed into teflon. As reference electrode silver chloride one was used, and as the support - the platinum electrode. Prior to determining the electrochemical characteristics of the electrode was polished on emery paper of different grits, degreased with acetone and kept for 3 days in a tightly closed container above the beaker with the liquid volatile inhibitor.

Results and Discussion

The results of accelerated corrosion tests are shown in Figure 1. Analysis of the results shows that the composition of volatile inhibitors designed based on vegetable raw materials ЛВГ-1 and ЛВГ-2 protect metal from corrosion when used as a contact method, and the substrate from the vapor phase and in the form of inhibited paper.

However, it should be noted that the effectiveness of the protective effect depends on the number of ways to use a volatile inhibitor. Thus, when contact applying the solution of the inhibitor protection of the metal is somewhat lower (80.8-93.4%) than the substrate composition of the vapor phase (98.3-98.8%) or in the form of paper of inhibited (94.95 - 94.14%). Apparently this is due to the fact that the extraction of plant material, except for volatile compounds with inhibitory ability in the composition contains non-volatile substances with increased aggressiveness in relation to the metal. Therefore, they are applied in contact, getting on the metal surface reduce the protective properties of the formed film. This, in turn, indicates the prospects of using these volatile fractions of the investigated plant materials.

At the same time, the results indicate that the proposed composition of volatile corrosion inhibitors, based on extracts of plant materials for application of the vapor phase, the contact method in the form of inhibited paper have higher protective properties than the standard НДА volatile inhibitor (**Figure 1a, b** and **c**).

Table 1. The results of accelerated tests

Inhibitor	Method of inhibitor application	Time of center appearance, days					Protection degree, %
		3	5	10	15	20	
ЛВГ-1	Contact application	-	-	-	-+	+	80.8
	Vapour phase	-	-	-	-	-+	98.3
	Inhibited paper	-	-	-	-	-+	94.9
ЛВГ-2	Contact application	-	-	-	-+	+	93.4
	Vapour phase	-	-	-	-	-+	98.8
	Inhibited paper	-	-	-	-	-	94.1
НДА	Vapour phase	-	-	-+	-+	+	89.7
	Inhibited paper	-	-	-	-+	+	93.1
Without inhibitor		-	-+	+	++	++	–

Note: [-+] – first appearance of corrosion; [+] – a small number of centers; [+] – a significant amount of corrosion centers

In the process of accelerated tests we assessed time of the first appearance of corrosion on the surface of the samples (**Table 1**). Analysis of the results shows that the volatile corrosion inhibitors to the extracts of plant materials provide more stable protection in the initial test period (up to 20 days). The first significant corrosion damage on the samples after treatment with inhibitors of volatiles from plant material from the vapor phase and in contact application appeared after an average of 15-20 days tests, which is 5-10 days later than the НДА.

In the case of using developed inhibitors ЛВГ-1 and ЛВГ-2 as inhibited paper for a longer period (60 days) the effectiveness of their actions are slightly higher than the НДА (**Figure 1c**). The results obtained show that the developed compositions have a high inhibitory capacity, especially in the early stages of the corrosion process unlike the НДА, the use of which the first centers appeared after 10 days tests. In the case of paper containing a corrosion inhibitor ЛВГ-1 (based on the hop cones), provides an effective protective action for 32 days The samples lose only slightly metallic sheen (**Figure 1c**).

The results of polarization studies Ст3 treated VCI from the vapor phase are presented in **Table 2**.

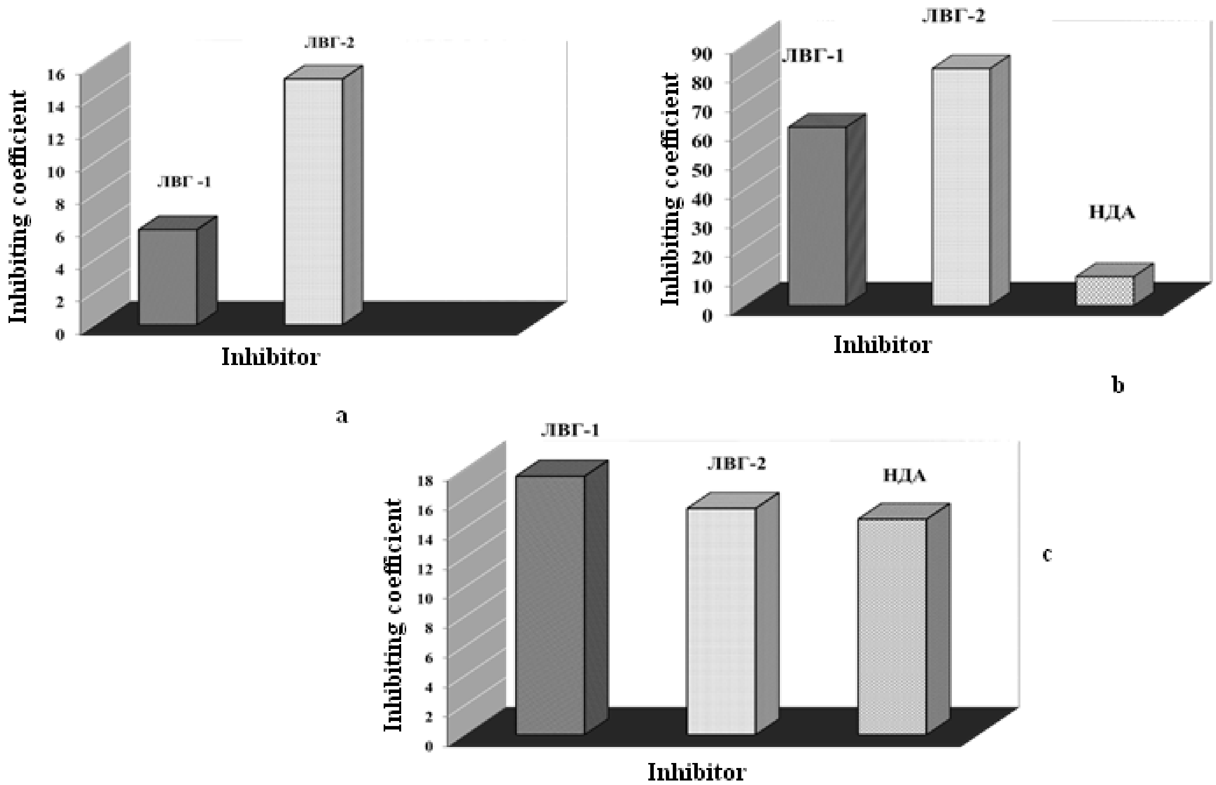

Figure 1. Inhibiting coefficient the corrosion rate of VCI during application by contact method (a) from the vapor phase (b), in the form in the form of inhibited paper (s)

Table 2. Results of treatment of anodic polarization curves of Ст3 after treatment with VCI

Inhibitor	Slightly aggressive atmosphere (1н Na_2SO_4)		Industrial atmosphere (distilled water + H_2SO_4, pH 2)		Marine environment (3 % NaCl)	
	*Km^-, g/m^2·h	**γ	Km^-, g/m^2·h	γ	Km^-, g/m^2·h	γ
ЛВГ-1	757.11	1.86	208.9	1.79	5373.5	1.26
НДА	922.7	1.52	268.6	1.39	5942.6	1.14
Without inhibitor	1405.7	-	374.4	-	6783.7	-

Note:

* The negative mass index Km^- (g/m^2·h) is defined at a potential of 1B metal corrosion rate of conversion formulas for the limiting current of dissolution on the polarization curves: $i = K_m^- \cdot \frac{n}{A} \cdot 2,68 \cdot 10^{-3}$, where i – current density of anodic dissolution (*A/cm^2*); n – valence of the metal ion passing into solution; 26,8 – Faraday constant (*A·h/g-eq*); A – atomic mass of metal.

** The braking rate of the anodic process γ is calculated from the formula $\gamma = \frac{i_0}{i_i}$, where i_0 and i_i – anode current density without inhibitor and with inhibitor, respectively. γ

Analysis of the results of electrochemical studies of the mechanism of action on the metal surface developed inhibitor ЛВГ-1, shows that they are effective in inhibiting the anodic process of corrosion of metal in neutral medium that simulates the slightly aggressive atmosphere, (γ = 1,86), and in an acidic medium, simulating acid atmospheric deposition (γ = 1,79), as well as in medium containing chloride ions, simulating the marine environment (γ = 1,26). Inhibitor НДА exhibits weaker inhibiting properties with respect to the proposed composition.

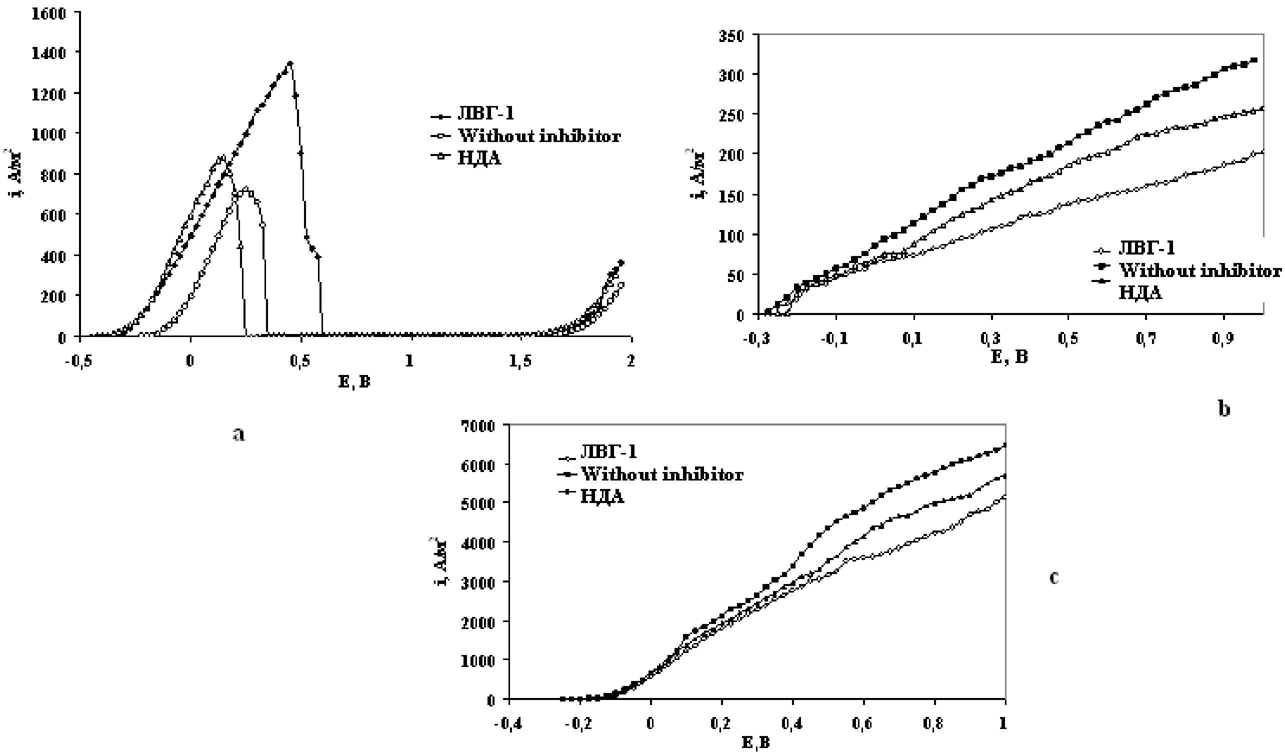

Figure 2. Anodic polarization curves of Ст3 treated with VCI in the vapor phase for 3 days in the environments simulating the corrosion process in a slightly aggressive atmosphere (a), industrial (b) and the marine atmosphere (c)

Conclusions

Developed on the basis plant raw materials volatile corrosion inhibitors ЛВГ-1 and ЛВГ-2 have a higher protective ability in comparison with a known inhibitor НДА.

More effective is the use them during application from the gas phase, as well as in the form of inhibited paper.

Inhibiting composition ЛВГ-1 inhibits the anodic reaction in slightly aggressive environment in 1.86 times in the industrial atmosphere - in a 1.79 times, the marine atmosphere - in 1.26 times.

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Исследование эффективности ингибиторов атмосферной коррозии

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Целью исследований явилась оценка эффективности разработанных летучих ингибиторов коррозии на основе растительного сырья. Установлено, что высокий уровень антикоррозионной защиты достигается при их использовании в виде ингибитированной бумаги и при нанесении из паровой фазы. Электрохимическими поляризационными методами исследований в модельных средах показано, что разработанные композиции превышают по защитным свойствами известный ингибитор НДА при использовании в условиях слабо агрессивной, промышленной и морской атмосферы.