Influence of cathode polarization on protective properties of thermoreactive coatings for main pipelines

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Abstract

The effect of cathodic polarization under cyclical temperature changing (from room temperature to 70 ^{o}C) on the protective properties of new and artificially aged heat-curing coatings for main pipelines has been investigated. It is shown that cathodic disbondment of coatings depends on their properties, temperature, applied potential. It has been established that the reducing (by absolute value) of the protective potential (with the IR component) from -1.45 to -0.75 V facilitate to retaining of the protective properties of coatings: the disbondment radius of a new hybrid-epoxide coating decreases in 3.3 times, aged coating – in 1.7 times, new and aged polyurethane coating – more than 20 times.

Keywords: *cathodic disbondment, cathodic polarization, hybrid-epoxide coating, polyurethane coating, protective potential.*

By this time in Ukraine more than forty thousand kilometers of operating main gas pipelines have been laid, mainly from pipes of large diameter (1220–1420 mm) and high working pressure of gas (up to 7.4 MPa). Gas pipelines are laid in different climatic conditions, with changes in topography of the area, different composition of soils, and so on. In practice, cases of breaking down of main gas pipelines are often caused by corrosion of the surface of the pipes, including stress corrosion cracking (SCC) [1].

Anticorrosion isolation and electrochemical protection are used to protect underground pipelines in the world, but it is impossible to protect metal pipes from the influence of the environment completely [1].

World experience [2] and the statistics of emergency damages caused by SCC show that the main gas pipelines with tape polymer coating are most subject to this kind of destruction, especially those in which the insulation was applied in field conditions.

The most effective method for reducing the probability of SCC is use of multifunctional isolation which is applied in the plant conditions and consists of several layers or contains ingredients, each of which has maximum protective properties from the influence of external factors, such as products of vital activity of sulfate-reducing bacteria, aggressive ions, water dissolved gases [3].

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Modern research analysis

Cathode polarization may have harmful effects if the protective potential goes beyond standard values. Experience has shown that the recommended values of the protective potential may sometimes be insufficient or excessive, which depends on the local properties of the environment. Cathodic polarization is a factor that can be practically managed [4].

Studies conducted by scientists at elevated temperatures (up to 150 °C) have demonstrated that cathodic disbondment depends both on the applied potential and conductivity, temperature, current density, thickness of the coating, composition of the solution, and the duration of the experiment [5]. With a large negative potential, the differences between individual results for all types of coatings are not sufficient and are within the accuracy of the method. Regardless of the applied potential, the polarization potential can not be lower than -1.2 V c.s.e. Therefore, an increase in the induced potential beyond a certain boundary does not lead to acceleration of testing [5].

There are experimentally confirmed data that the radius of disbondment increases with the increase of the temperature, the duration of the experiment, and a decrease in the thickness of the coating. Practical value and interest has the boundary to which these factors remain valid, and the nature of their interaction [6].

In some papers it has been noted that the disbondment of the coatings may be accompanied by the formation of rings of different colors on the surface of the steel. Their quantity, size, intensity and color depend not only on the degree of disbondment and temperature, but also on the type of electrolyte, the thickness of the coating, preliminary surface treatment, and, probably, on the properties of the coating [6]. The presence of rings of different colors (colors of variability) is explained by the difference in stoichiometry of compounds formed at different pH, potential, thickness of the coating. Taking into account that the components of the medium can diffuse through the film, it can be assumed that in front of the "common disbondment front" there is an area of less negative potential, which is gradually activated by a medium diffusing from the volume of the electrolyte. As a result, on the small areas of the coating, the adhesion of the cover with the substrate decreases, and then these areas merge with the front of the disbondment, which begins with the defect in the coating [6].

In papers [7, 8], concerning the effect of cathodic polarization on bitumen and tape coatings, it was indicated that with the deterioration of the insulation state, it is advisable to reduce the upper level of the potential to -1.20 V and simultaneously introduce additional electrochemical protection means (protector, cathode station) .

The effectiveness of decreasing of protective potential was proved in our previous research paper [9] for tape coating. It has been demonstrated that cathodic disbondment of tape coating (new and aged) depends on its properties, temperature, applied potential. It was established that the decrease (in absolute value) of the protective potential with an ohmic component from -1.45 to -0.80 V slows down the disbondment of coating with different degrees of aging: at room temperature – 6 times (new and aged), at a cyclic temperature change – 9 times (new) and 26 times (aged).

New modern materials on the epoxy and polyurethane basis appear on the market. The advantage of such coatings is high physical, mechanical and protective characteristics, and the coatings themselves are classified as class B (very reinforced) in accordance with DSTU 4219–2003 [10]. These coatings, including polyurethane WG-Welepipe (Ukraine), Sigmaline 855 (Belgium), IAMPROOF 302 (Italy), Carboline Polyclad 777 (USA), etc., are recommended for use primarily in corrosive and potentially stress-corrosion dangerous areas and are included into the Register of insulating materials and protective coatings on their basis, that can be used at the facilities of GTS PJSC "UKRTRANSGAZ". Any coating is expected to be ageing and this process can be accelerated under the influence of the external environment and cathode polarization

Many researchers are asking: what is the optimum potential of cathodic protection and how does excessive potential affect the coating?

Therefore, it was interesting to establish how cathodic polarization affects the newest coatings with a defect. To find out the influence of cathodic polarization on the protective properties of the thermosetting coatings of a new generation, on the basis of the modern research analysis, the purpose of the work was formulated, which was to compare the stability of the coatings (in the initial state and aged during 1000 hours at a temperature of 50 °C) under the effect of cathodic polarization at different protective potentials and cyclical temperature changes from room temperature up to 70 °C.

Materials and methods of researches

To study the influence of the cathodic polarization on the disbondment of protective polymer coatings applied to surface of X70 pipe steels, the method of cathodic disbondment control on the basis of the standard method according to DSTU 4219–2003 [10] has been used. The boundary conditions of electrochemical protection, such as the maximum and minimum protective potentials with the ohmic component: -1.45 and -0.75 V relative to chloride silver electrode (ch.s.e.) (-1.55 and -0.85 V relative to copper sulfate electrode) have been simulated. That made it possible to obtain polarization potentials close to the maximum and minimum protective ones: -1.05 and -0.75 V ch.s.e., respectively.

To maintain the potential, a magnesium anode was used with a potential of -1.45 to -1.55 V ch.s.e. Due to the fact that the expected polarization currents are small, a laboratory stand based on the clamping electrochemical cell (1), described in detail in [9], was developed for research, equipped with a multichannel potentiostatic device (2) for controlling the protective potential in the cell, measuring instruments (voltmeter-ammeter and microammeter with a range of measurement of currents from 0 to 20 mA) (Fig. 1).

Cathodic disbondment of coating was carried out in a clamping cell, Fig. 1 (1) at applied potentials (with IR-drop) -1.45 and -0.75 V relative to ch.s.e. The thermosetting single-layer coatings of the new generation with 100 % dry residue were used: hybrid epoxy and polyurethane by the thickness of 1.2 and 2 mm, respectively. The coatings are applied in field conditions to samples of X70 pipe steel (100×100) mm after sand blasting. An artificial defect with a diameter of 6 mm was made in the coating. The coatings were investigated in the initial state and after aging, which was carried out by holding them at a temperature of 50 °C for 1000 hours.

The cell was filled with a solution of 3 % NaCl in a volume of 250 ml.

The research was carried out at a cyclic temperature change, namely:

at the room temperature – for 4.5 days a week;

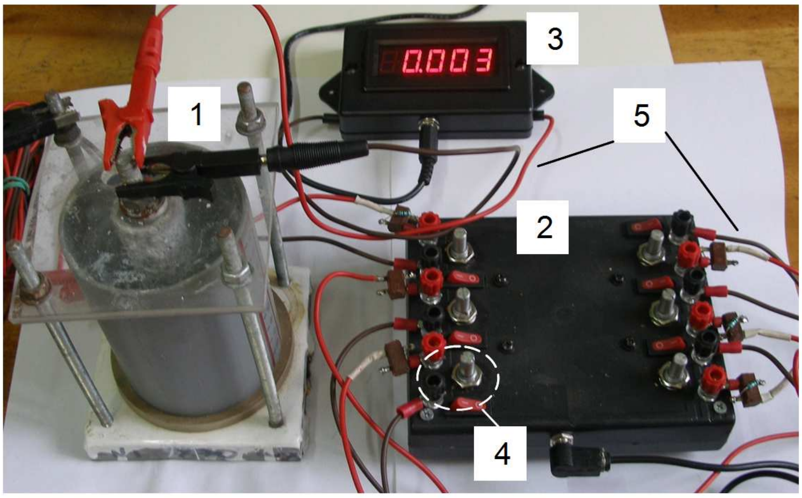
at 50 or 70 °C – for 2.5 days a week.

The hybrid epoxy coating was being exposed for 1 month at a temperature of 50 °C and for 4 months at a temperature of 70 °C, polyurethane – for 2 months at a temperature of 70 °C.

During the study under applied potentials, the protective potential with IR-drop, polarization potential and polarization current were measured. It should be noted that at the potential -0.75 V (ch.s.e.) the polarization potential approaches the potential with IR-drop, therefore only the potential with the IR-drop was controlled. After research, the radius of disbondment of coating was determined.

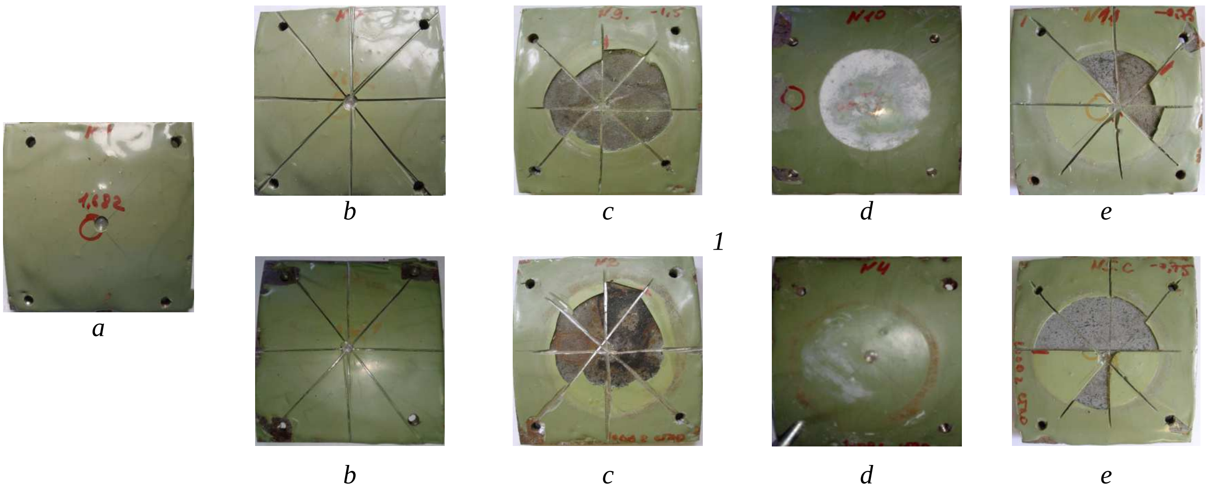
Investigation of the influence of cathodic polarization on the protective properties of the hybrid epoxy coating

Fig. 2 shows photo of samples after testing at different potentials, in Fig. 3 – the change of



1 – a clamping cell; 2 – multichannel potentiostatic device;
3 – microammeter; 4 – channel to connect the cell; 5 – connecting wires

Figure 1 – Laboratory bench for research of cathodic disbondment of protective polymer coatings



a – before the test; b, c – after capacity tests -1.45 V for 1 (b) and 4 months (c);
d, e – after capacity tests -0.75 V for 1 (d) and 4 (e) months

Figure 2 – The appearance of a new (1) and artificially aged (2) epoxy coating after the influence of cathodic polarization during cyclic temperature changes

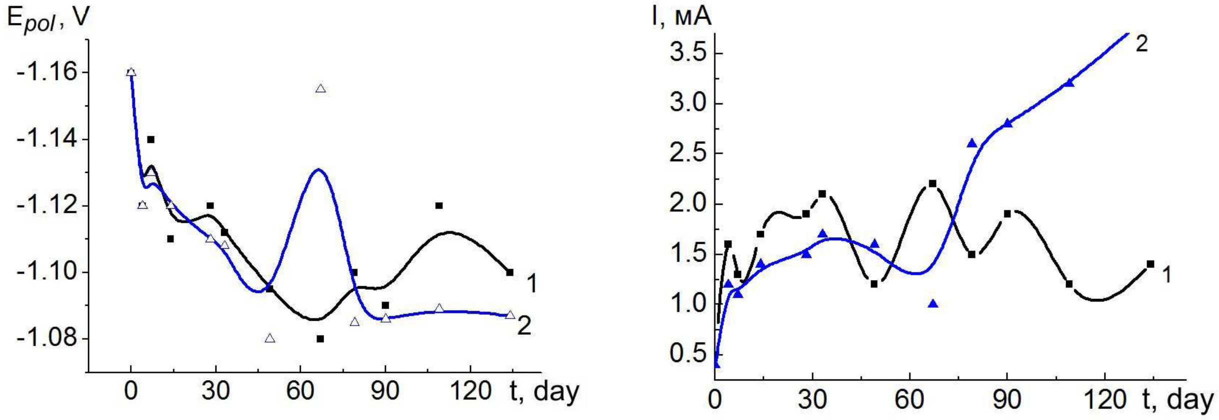
polarization potentials and currents during tests under the potential with IR-drop -1.45 V. From the Fig. 3 it is clear that the polarization potentials changed nonmonotonically and were shifted towards more positive values with an increasing of temperature to 70 °C (after 60 days). During the first month of the test (Fig. 3, *b*) at a temperature of 50 °C, the polarization currents on both samples did not exceed 2.2 mA. With an increasing of the temperature up to 70 °C, polarization currents on samples with aged coating increased almost twice and reached 3.9 mA (Table 1). The maximum radius of disbondment of coating under this potential was 22.9 mm, both for the new and for the aged coating.

At applied potential -0.75 V, after 1 month of testing white sediments, presumably magnesium salts, appeared on the surface and easy removed by a soft sponge (Fig. 2) (photo 1, *d* and 2, *d*).

It has been assumed that the deposition of these salts and their sufficiently strong adhesion to the coating runs precisely under the potentials close to the minimum protective potential, since under the potentials of -1.45 V, this phenomenon was not observed.

At the end of the testing, the radius of the disbondment of the new coating was 6.9 mm while that of the aged coating was 13.1 mm. In such a way, the reduction of the protective potential from -1.45 V to -0.75 V promote to slowing disbondment of the new coating (in proportion to the radius of disbondment) by 3 times, of the aged coating – by 1.7 times.

It should be noted that the protective potential -0.75 V practically coincides with the values of polarization potential. At the end of the test, the polarization currents were about 0.095 μA on the sample with a new coating and 0.112 μA on the sample with the aged coating (Table 1).

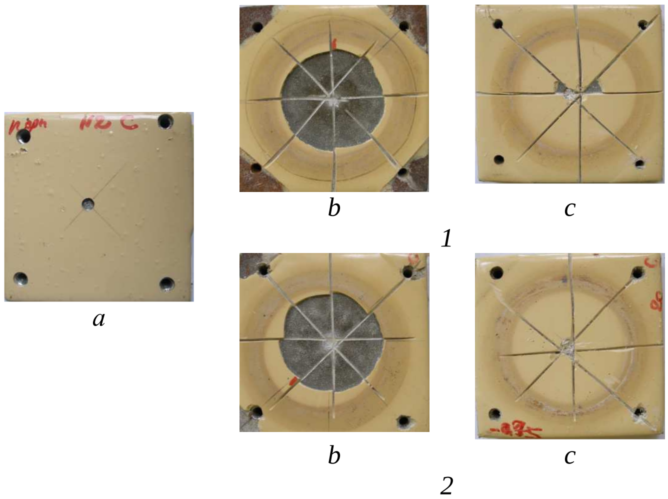


a *b*

Figure 3 – Change of polarization potential (*a*) and current (*b*) for 4 months during cyclic change of temperatures at the potential -1.45 V during the study of cathodic disbondment of a new (1) and aged (2) hybrid epoxy coating

Table 1 – Polarization characteristics of disbondment process of protective hybrid epoxy coating, applied to X70 steel

Type of coating	Protective potential with an IR-drop, V	Polarization potential, V	Polarization current, A
New	-1.427	-1.100	$1.4\cdot10^{-3}$
	-0.750	-0.750	$9.5\cdot10^{-8}$
Artificially aged	-1.432	-1.087	$3.9\cdot10^{-3}$
	-0.750	-0.750	$1.12\cdot10^{-7}$



a – before the test; b – after testing at potential -1.45 V; c – after testing at potential -0.75 V

Figure 4 – The appearance of new (1) and artificially aged (2) polyurethane coating after the influence of cathodic polarization during a cyclic change of temperature for 2 months

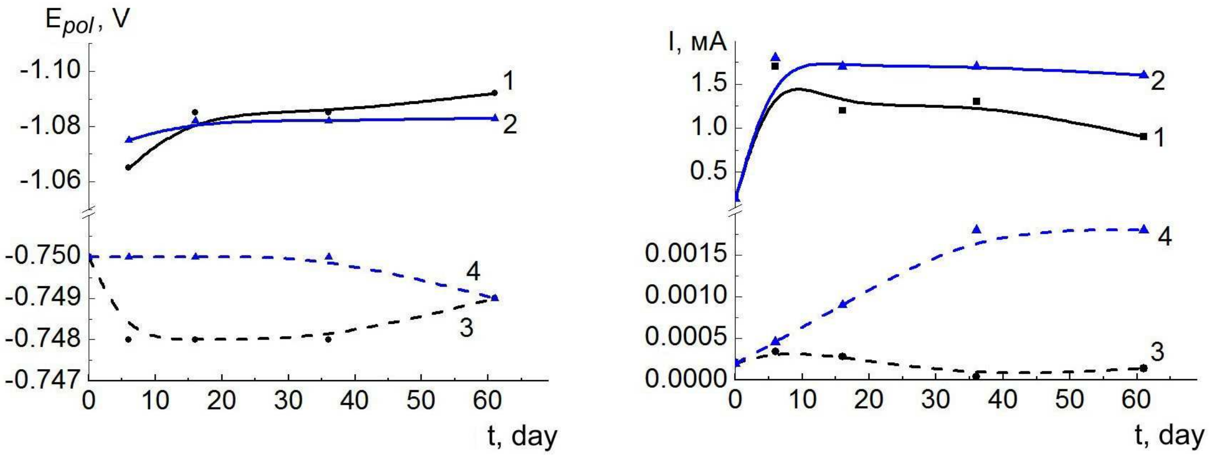
Thus, at cathodic polarization -1.45 V, the artificial aging of the epoxy coating practically did not affect its disbondment at elevated temperatures during 4 months. Reducing the level of cathodic polarization to -0.75 V (ch.s.e.) promote to slowing disbondment of both new and aged coatings, and for the new coating, this effect was greater.

Fig. 4 shows a photo of the appearance of the coating before and after the testing. For this coating, the effect of cyclic temperature changes without polarization has been investigated and it has been found that there was no disbondment of coating, the radius was zero.

Investigation of the influence of cathodic polarization on the protective properties of polyurethane coating

As you can see in Fig. 4 (photos 1, *b* and 2, *b*) there was a very small difference between the radius of disbondment of new and aged coatings (21.9 mm and 20.4 mm respectively) for cathodic polarization at -1.45 V.

Fig. 5, *a* (curves 1, 2) demonstrates changing of polarization potentials at a protective potential with an IR-drop and polarization currents, Fig. 5, *b* (curves 1, 2). It can be seen that for new and aged



a *b*

1, 3 – new coating; 2, 4 – artificially aged coating

Figure 5 – Change of the polarization potential (*a*) and current (*b*) at the cyclic change of the temperatures at the potential of -1.45 V (1, 2) and -0.75 V (3, 4) during the study of the cathodic disbondment of the new and aged polyurethane coating for 2 months

Table 2 – Polarization characteristics of the disbondment process of protective polyurethane coating applied to X70 steel

Type of coating	Protective potential with an IR-drop, V	Polarization potential, V	Polarization current, A
New	-1.427	-1.100	$1.4 \cdot 10^{-3}$
	-0.750	-0.750	$3.4 \cdot 10^{-7}$
Artificially aged	-1.432	-1.087	$3.9 \cdot 10^{-3}$
	-0.750	-0.750	$1.8 \cdot 10^{-6}$

coatings polarization potentials and currents slightly differ (Table 2), which is confirmed by their radii of the disbondment, the differences between which are insignificant.

In Fig. 5 (curves 3, 4) changing of polarization potentials at protective potential close to the minimum value -0.75 V (ch.s.e.), and currents at cyclic temperature changing (70 °C) is shown. From Fig. 5 (curves 3, 4) and Table 2 it is evident that the polarization potential on samples with new and aged coating slightly varied and practically coincided with the applied potential -0.75 V, while the maximum polarization currents reached the values of 0.34 μA for a sample with a new coating, and 1.8 μA – with the aged coating, that is 3-4 times less than at the polarization value of -1.45 V (not more than 1.8 mA). The radii of disbondment in both cases were 0, Fig. 4 (photo 1, *c* and 2, *c*).

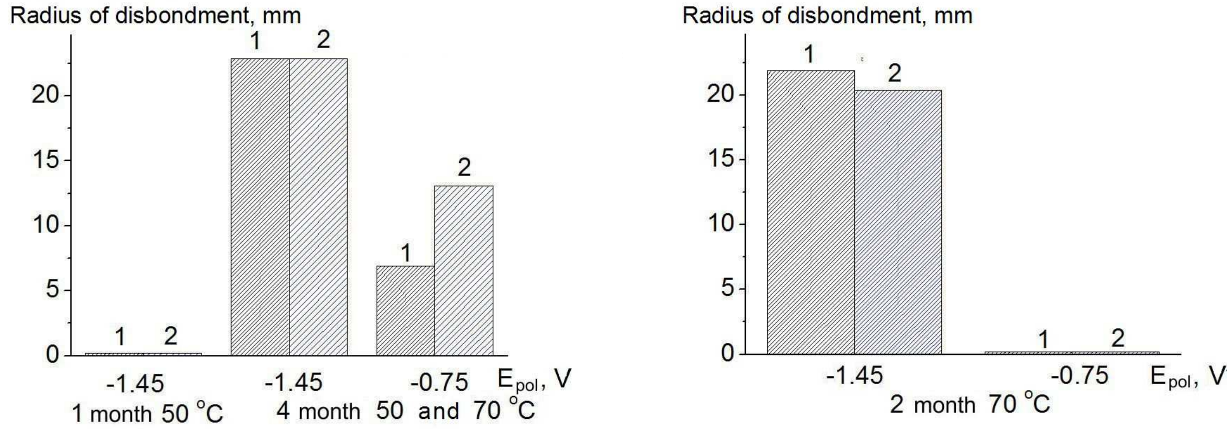
Reducing the protective potential to -0.75 V practically stopped the disbondment, Fig. 4 (photo 1, *c* and 2, *c*). Since a similar effect was observed without polarization, it can be assumed that the cyclic change in temperature (from room temperature to 70 °C) practically does not affect the polyurethane coating (new and artificially aged). Reducing the level of cathode polarization from the maximum protective potential to the minimum (-0.75 V) has made it possible to avoid the disbondment of the polyurethane coating at elevated temperatures.

Taking into account the obtained data for this class of coatings, it is expedient to investigate the possibility of their application without cathodic polarization in natural conditions.

After studying the stability of the coatings of different structures against cathodic disbondment on the bare surface of the metal, the formation of rings of dark color was observed (Fig. 4 (photo 1, *b* and 2, *b*)), sometimes of different shades. A similar phenomenon was observed by other researchers [6] who noticed that the size and color of such rings depended on the degree of disbondment, the properties of the coating, the temperature, the composition of the electrolyte, and the preparation of the surface. They associate a change in the color of the ring with a different chemical composition of compounds, the formation of which is due to the joint action of cathode polarization, pH and elements that are parts of the coating.

Some researchers [11] suggested that there is an oxide film on the boundary between the coating and the steel prior to cathodic disbondment, which may contain Fe_2O_3 and Fe_3O_4 before disbondment, and in the presence of moisture, it may contain small amounts of $Fe(OH)_2$, $Fe(OH)_3$, FeOOH and $FeCO_3$ (such an oxide film may be called interphase to make it easier). The mechanism of cathodic disbondment of the coating from the metal surface may include electrochemical reviving of Fe_2O_3 in the interphase oxide film.

It has been assumed that when the surface is exposed under the disbonded coating, the interphase oxide film begins to recover at potentials approaching the polarization potential of -1.05 V (ch.s.e.), in accordance with the reaction:



a *b*

1 – new coating; 2 – artificially aged coating

Figure 6 – The radius of disbondment of a new (1) and aged (2) epoxy (*a*) and polyurethane (*b*) coatings at a cyclic changing of temperature from room temperature to 70 °C for potentials of cathodic polarization of -1.45 and -0.75 V in 1 and 4 months of exposure

$$Fe_3O_4 + 2H_2O + 2e^- \rightarrow 3HFeO_2^- + H^+,$$

which initiates cathodic disbondment.

As a result of the analysis of the potential-pH diagram for the Fe–CO_2–H_2O system at 60 °C, the $HFeO_2$ ion is stable in the presence of an alkaline medium formed as a result of the decomposition of the aqueous electrolyte by cathodic polarization and impregnates under the coating. The recovery of Fe_3O_4 in the interphase oxide film runs on beyond the limiting potential of the cathodic protection approaching the maximum polarization. The electrocapillary process reduces the surface tension on the boundary of the steel / crevice solution under the coating. These two components of the mechanism lead to a violation of the relationship between the adhesive component of the coating and the steel surface, and, as a result, the coating is being disbonded from steel [11].

Thus, it can be assumed that the rings formed on the surface during the disbondment are products of the recovery of the interphase oxide and components of the coating layer, which directly contacts with the surface of the metal.

From the analysis of experimental data it was established that during the cyclic temperature changing, the radii of the new and aged coatings as hybrid epoxy and polyurethane were practically the same or differed under some conditions of the test (Fig. 6).

Probably, over time, you should expect a faster increase in the radius of disbondment of the sample with the aged coating than with the new one.

For the aged polyurethane coating, a slight decrease in the radius of disbondment (20.4 mm) was observed compared to the new one (21.9 mm), which is about 7 %. This is probably due to the properties of the coating material.

Thus, the decreasing (in absolute value) of the protective potential promotes the preservation of protective properties of thermosetting coatings. It is right to assume that this effect will be intensified over time in the course of pipelines operation.

Conclusions

Cathodic disbondment of protective thermosetting coatings depends on the applied potential, temperature, duration of exposure. With a large negative potential, the differences for the different types of coatings (new and aged) are negligible.

The study of the influence of cathodic polarization at the potentials of -1.45 and -0.75 V (ch.s.e.) on the protective properties of the new and old thermosetting coatings showed the following:

the artificial aging of the hybrid-epoxy coating at the cathodic polarization of -1.45 V (ch.s.e.) practically does not affect its protective properties at elevated temperatures. Reducing cathodic polarization to a minimum protective potential of -0.75 V promotes to slowing down the disbondment of both new and aged coatings. For a new coating, this effect is more sufficient;

reducing the protective potential to a minimum of -0.75 V virtually halts the disbondment of the polyurethane coating at elevated temperatures. Since a similar effect was observed without polarization, it was assumed that the temperature change from room temperature to 70 °C practically does not affect its disbondment. Taking into account the obtained data for this class of coatings, it is expedient to investigate the possibility of their application without cathodic polarization in the natural conditions depending on the properties of the environment.

At a cyclic changing of temperature (from room temperature to 70 °C), the reducing of the protective potential with IR-drop from -1.45 to -0.75 V helps to preserve the protective properties of thermosetting coatings by the index of the radius of disbondment: the new hybrid-epoxy – in 3.3 times, the aged one – in 1.7 times after 4 months of the exposure; new and oldest polyurethane in more than 20 times after 2 months of the exposure.

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УДК 620.197.5

Вплив катодної поляризації на захисні властивості термореактивних покривів для магістральних трубопроводів

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Досліджено вплив катодної поляризації за циклічної зміни температур (від кімнатної до 70 ^{o}C) на захисні властивості нових та штучно зістарених термореактивних покривів для магістральних трубопроводів. Показано, що катодне відшарування покривів залежить від їх властивостей, температури, наведеного потенціалу. Встановлено, що зниження (за абсолютним значенням) захисного потенціалу з омічною складовою від -1.45 до -0.75 В сприяє збереженню захисних властивостей покривів: радіус відшарування нового гібрид-епоксидного зменшується в 3.3, зістареного – в 1.7 разів; нового та зістареного поліуретанового – більше ніж у 20 разів.

Ключові слова: *гібрид-епоксидний покрив, захисний потенціал, катодна поляризація, катодне відшарування, поліуретановий покрив.*