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# MICROBIAL CORROSION OF PROTECTIVE COATINGS

Zh. P. Kopteva, V. V. Zanina and I. A. Kozlova

Research studies have shown that protective coatings of diverse chemical composition represent a powerful factor stimulating the bacterial activity of corrosion inducers. On the film and mastic coatings investigated in the present paper, bacterial communities are formed, which consist of bacteria of various ecological trophic groups. Bacteria in a biofilm are characterised by high metabolic activity and the ability to destroy traditional coatings. As a result of microbial destruction, the physical mechanical and chemical properties of a material undergo significant changes. The characteristics of strength, elasticity and adhesion deteriorate, thus degrading the main function of the coatings, i.e. protection of metal against corrosion. An efficient method of protection against biodeterioration is the addition of corrosion inhibitors with biocide action into their composition. It was established that the population of bacteria on oil bitumen coatings modified by antimicrobial bonds is 1–4 orders lower than on materials

with no such additives. Protection of underground structures against corrosion should be performed comprehensively with consideration of the biocorrosivity of soils and bioresistance of coatings. SE/S294

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**Keywords:** Microbial corrosion, Protective coatings, Adhesion, Biofilm, Bacteria destructors, Physical-mechanical properties, Bioresistance, Corrosion inhibitors

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## INTRODUCTION

Coatings applied to protect metal and metal construction from corrosion present a special environment for micro-organisms. For each coating material, a microbial community has formed with a unique composition and number of micro-organisms between which close functional relationships are established.

There is little literature available concerning the composition of micro-organisms forming a biofilm on materials that protect pipelines from corrosion. In 1963, Harris<sup>1</sup> has described the participation of soil bacteria, namely sulphate reducing bacteria, in the deterioration of corrosion resistant coatings on oil and gas pipelines. According to results on polymeric coatings based on polyethylene and a polyvinylchloride obtained by other researchers,<sup>2,3</sup> there are also bacteria of other taxonomic groups: *Pseudomonas aeruginosa*, *Ps. herbicola*, *Ps. fluorescens*, *Ps. resinovorans*, *Bacillus subtilis*, actinomycetes, as well as micromycetes. Williams<sup>4</sup> has specified that actinomycetes participate at later stages of the destruction process, when there are compounds left that are hard to reach for other groups of micro-organisms. Some features of these are slow growth and high resistance to unfavourable environmental factors. Therefore, as noted by Lugauskas *et al.*<sup>5</sup> after they started colonisation on polymeric materials, they survive there for a very long time. On these materials there are streptomycetes: representatives of *Globisporus*, *Albus*, *Griseus*, *Rubro aurantiacus* and *Olivaceus* groups. Hard to reach compounds, when transformed by streptomycetes, can become a source of nutrition for other groups of micro-organisms. Therefore, after augmentation of the number of active streptomycetes, augmentation of the number

of bacteria of different taxonomic groups is also observed.

It is known that, during their growth and development, micro-organisms evolve organic and mineral acids, and a number of enzymes. Solutions of organic and mineral acids appear as corrosive media during biodeterioration of insulants. By means of enzymes, micro-organisms provide oxidation, reduction and other reactions, which erode low polymeric fractions of polyethylene and polyvinylchloride and another component of coatings, acyclic and aromatic hydrocarbons, which are part of some bitumens, as well as other ingredients of coatings.<sup>6</sup>

## EXPERIMENTAL

### Protective materials

The effects of modified oil bitumen on the population growth of corrosion aggressive micro-organisms was studied. Commercial products and waste products of large capacity chemical and petrochemical plants were used as modifiers.

Oil bitumen materials and their modifications were obtained from the Institute of Physical Mechanics, National Academy of Sciences of Ukraine.

Materials used in the experiments were as follows:

- (i) Polyken 980-25 (PE)
- (ii) polyvinylchloride (PVC)
- (iii) polyurethane (PU)
- (iv) coal mastic (Katizol)
- (v) oil bitumen (BNI-IV)
- (vi) bitumen rubber mastic (MBR-90)
- (vii) kukersite base (OK)
- (viii) bitumen–latex–kukersite mastic (BLK)
- (ix) still bottom after rectification of synthetic fatty acids (KO SZhK)

- (x) ground Carpathian shale (MKS)
- (xi) road oil (MD)
- (xii) a shale oil fraction (SF)
- (xiii) BNI-IV, OK
- (xiv) BNI-IV, BLK
- (xv) BNI-IV, KO SZhK
- (xvi) BNI-IV, MKS
- (xvii) BNI-IV, MD
- (xviii) BNI-IV, SF
- (xix) MBR-90, KHO-1
- (xx) MBR-90, KHO-2
- (xxi) MBR-90, KHO-3
- (xxii) MBR-90, KHO-4.

### Testing of physical and mechanical properties of coatings

The state of the coatings, the formation of biofilm on the coating surface and the physical and mechanical properties of the materials were monitored during the experiment.

Rupture strength, specific elongation and adhesive strength were tested by GOST 14236-81, GOST 28840-90 and GOST 30738-2001.<sup>7-9</sup>

### Microbiological analyses

Bacteria were enumerated by the method of serially diluting to extinction in liquid media. Denitrifying bacteria (DNB) were grown in Hiltay medium, sulphate reducing bacteria (SRB) in Postgate B medium, iron reducing bacteria (IRB) in Kalynenko medium, hydrocarbon oxidising bacteria (HCOB) in Tauson medium, thionic bacteria (TB) in Beijerinck media and ammonifying bacteria (AMB) in beef-peptone broth.<sup>10,11</sup> Microbial communities on the coatings were studied by replica plating methods.<sup>12</sup> Bacteria isolated from coatings were enumerated in liquid media using the MPN technique. Cells were washed off the coatings with sterile water before inoculation into DNB, SRB, IRB, HCOB, AMB and TB media.

### Bacteria adhesion to protective coatings

Coating specimens (20–30 mm for Polyken 980-25 and 10–10 mm for oil bitumen coatings) were submerged into bacteria suspension for 5 and 60 min, then washed in 0.01M phosphate buffer.

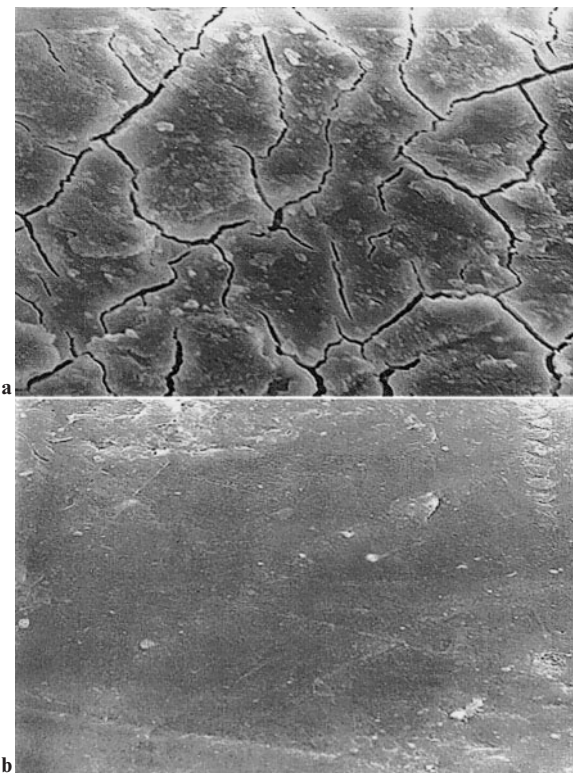
The number of adherent bacteria cells was tested by direct account method under the microscope (Brid method).<sup>13</sup>

The adhesion number was calculated by the formula<sup>14</sup>

$$A = \frac{N \times 100}{N_0} \quad \dots \dots \dots (1)$$

where  $A$  is the adhesion number, %,  $N$  is the number of adhesion cells, and  $N_0$  is the number of free swimming cells in the media.

The initial material for isolation of extracellular polysaccharides was the cultural liquid obtained after removal of microbial cells by centrifugation (10 000g, 30–60 min). The supernatants were used to isolate the polysaccharides and their precipitation by 3 vol.-% acetone at 0–4°C. Precipitated polysaccharides were separated by centrifugation, washed several times in acetone and dried in a vacuum.<sup>15</sup>



*a* deteriorated,  $\times 600$ ; *b* non-deteriorated, SEM,  $\times 600$

1 Surface of Polyken 980-25

The monosaccharide composition of the isolated polysaccharides was investigated after hydrolysis by 1N HCl at 100°C for 3 h. Then the samples were acetylated and analysed using a Specol-11 gas-liquid chromatograph.<sup>15</sup>

### Bacteria hydrophobicity testing

The method is based on the property of micro-organisms possessing of the hydrophobic zones on their surface to adhere to the hydrocarbons.<sup>16</sup>

### $\xi$ potential bacteria cell testing

The  $\xi$  potential or electrokinetic bacteria cell charge was tested by the micro-electrophoretics method. On the electrophoresis design, the rate of electrophoresis of 50–100 cells was tested, and the potential was estimated.<sup>17</sup>

### Bacterial aggressive metabolites testing

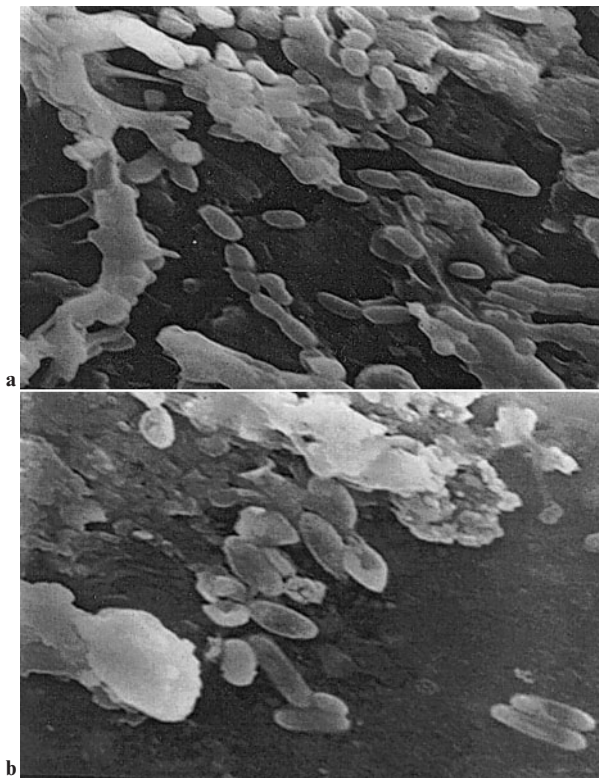
Nitrates were tested in the cultural liquid of the DNB colorimetrically with disulphophenolic acid.<sup>18</sup>

Hydrogen disulphide was tested in the cultural liquid of the SRB iodometrically.<sup>19</sup>

The bactericidity of the coating components and the coating bioresistance were tested by GOST 30738-2001.<sup>9</sup>

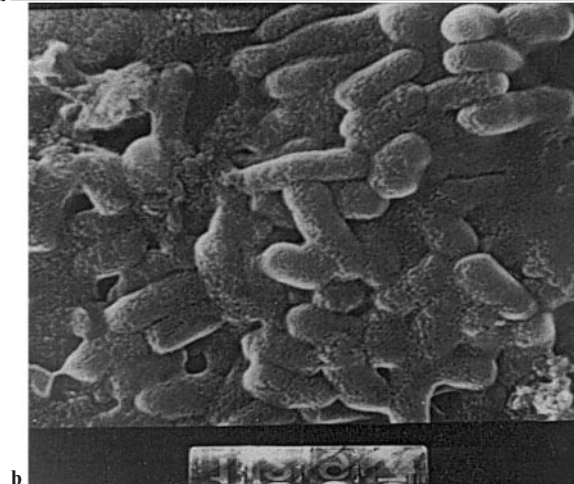
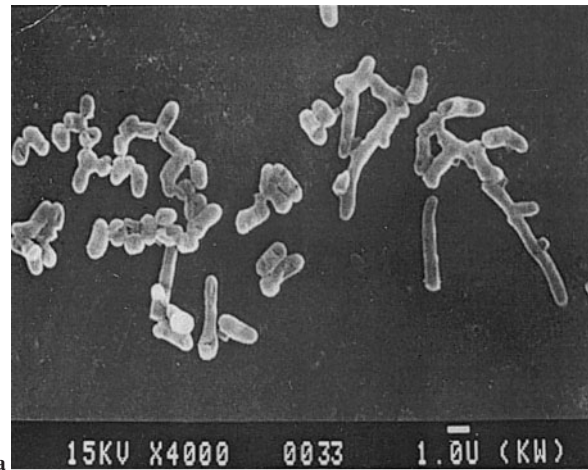
## RESULTS AND DISCUSSION

As a result of ecological investigations performed by the present authors in the defective film and the bitumen coatings sampled during a diagnostic study of gas main pipelines and underground reservoirs, bacteria of different ecological-trophic groups were identified (see Figs. 1 and 2).

a  $\times 6000$ ; b  $\times 6000$ **2** Bacteria biofilms on surface of Polyken 980-25 of main gas pipelines, SEM

A biofilm is formed on the surface of all the investigated material by IRB, DNB, HCOB and SRB. It is noteworthy that TB appear only on polyvinylchloride and bituminous coatings which protect underground reservoirs. The number of isolated bacteria in a biofilm formed on the defective coatings is 1–4 orders higher on oil bitumen materials (BNI-IV) than on polyethylene and polyvinylchloride coatings (Table 1).

In laboratory test conditions, the bacterial film on the surface of insulating coatings is formed mainly within 14 days (see Tables 2 and 3 and Fig. 3). The bacteria isolated from the biofilm are characterised by high denitrifying and sulphate reducing activities, which result in the formation of aggressive metabolites,  $\text{NO}_2$ ,  $\text{NH}_3$  and  $\text{H}_2\text{S}$ , which have an influence on the processes occurring on the surface of protective materials. Three days after the test, denitrifiers restored up to 57% of the nitrates added to the nutrient medium. Protective materials had diverse effects on the activity of the cultures. Polyethylene and polyurethane provided an insignificant inhibitive effect on the restoration of nitrates. In the presence of BNI-IV coating, stimulation of this process was observed. The same coating modified by corrosion

a DNB  $\times 4000$ ; b HCOB  $\times 10\,000$ **3** Biofilms of DNB and HCOB on surface of Polyken 980-25, SEM

inhibitors, biocides OK and BLK, depressed the denitrifying activity of bacteria by 53.6–60.7%.

The SRB which were introduced in the test formed 42.5–272 mg hydrogen sulphide per litre of medium during the 14 day test (Table 4). In the presence of the investigated coatings, the sulphate reducing process is depressed. For example, BNI-IV, OK and BNI-IV, BLK coatings caused the reduction of  $\text{H}_2\text{S}$

**Table 2** Number of AMB on surface of protection coating, cells  $\text{cm}^{-2}$  surface

| Experiment     | Exposition, days  |                   |                   |                   |                   |
|----------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|                | 1                 | 3                 | 7                 | 14                | 21                |
| Polyken 980-25 | $7.0 \times 10^5$ | $7.0 \times 10^6$ | $6.0 \times 10^6$ | $7.0 \times 10^7$ | $1.3 \times 10^7$ |
| BNI-IV         | $1.0 \times 10^5$ | $6.0 \times 10^5$ | $1.3 \times 10^6$ | $6.0 \times 10^7$ | $2.5 \times 10^6$ |
| BNI-IV, OK     | $1.3 \times 10^3$ | $1.1 \times 10^4$ | $6.0 \times 10^4$ | $1.1 \times 10^5$ | $6.0 \times 10^4$ |
| BNI-IV, BLK    | $1.3 \times 10^3$ | $2.5 \times 10^4$ | $6.0 \times 10^4$ | $2.5 \times 10^5$ | $6.0 \times 10^4$ |
| Polyurethane   | $1.1 \times 10^4$ | $6.0 \times 10^5$ | $2.5 \times 10^6$ | $6.0 \times 10^7$ | $7.0 \times 10^5$ |

**Table 1** Number of bacteria in biofilm on surface of defective coatings per 1 g bituminous coating or per 1  $\text{cm}^2$  film coating

| Coating type      | Sampling site          | Iron reducing bacteria | Denitrifying bacteria | Hydrocarbon oxidising bacteria | Sulphate reducing bacteria | Thionic Bacteria |
|-------------------|------------------------|------------------------|-----------------------|--------------------------------|----------------------------|------------------|
| Bitumen BNI-IV    | Gas pipelines          | $10^3$ – $10^6$        | $10^3$ – $10^2$       | $10^2$ – $10^6$                | $10^2$ – $10^6$            | 0                |
| Bitumen BNI-IV    | Underground reservoirs | $10^5$ – $10^9$        | $10^2$ – $10^9$       | $10^1$ – $10^8$                | $10^1$ – $10^6$            | $10^1$ – $10^3$  |
| Polyethylene      | Gas pipelines          | $10^2$ – $10^5$        | $10^3$ – $10^5$       | $10^2$ – $10^3$                | $10^1$ – $10^4$            | 0                |
| Polyvinylchloride | Gas pipelines          | $10^5$ – $10^7$        | $10^3$ – $10^6$       | $10^2$ – $10^3$                | $10^3$ – $10^4$            | $10^1$ – $10^2$  |

**Table 3** Number of HCOB on protection coatings surface, cells cm<sup>-2</sup> surface

| Experiment     | Exposition, days  |                   |                   |                   |                   |
|----------------|-------------------|-------------------|-------------------|-------------------|-------------------|
|                | 1                 | 3                 | 7                 | 14                | 21                |
| Polyken 980-25 | $1.3 \times 10^2$ | $2.5 \times 10^3$ | $6.0 \times 10^4$ | $7.0 \times 10^5$ | $1.3 \times 10^4$ |
| BNI-IV         | $2.5 \times 10^3$ | $6.0 \times 10^3$ | $6.0 \times 10^4$ | $2.5 \times 10^5$ | $2.5 \times 10^4$ |
| BNI-IV, OK     | $0.6 \times 10^2$ | $2.5 \times 10^2$ | $1.1 \times 10^3$ | $2.5 \times 10^3$ | $1.3 \times 10^3$ |
| BNI-IV, BLK    | $1.1 \times 10^3$ | $6.0 \times 10^3$ | $1.3 \times 10^3$ | $1.3 \times 10^4$ | $6.0 \times 10^3$ |
| Polyurethane   | $1.1 \times 10^3$ | $2.5 \times 10^4$ | $6.0 \times 10^4$ | $1.3 \times 10^5$ | $6.0 \times 10^4$ |

formation by a factor of 1.6–2.8. Coating BNI-IV with no modifying additives had essentially no effect on H<sub>2</sub>S formation by SRB.

Under the effect of DNB and SRB, the polymer coating durability dropped: specific elongation, 19%; rupture strength, 37%. After exposure to the coating, the samples showed degradation of their glue base. For example, the DNB and SRB aggregates reduce the adhesive strength of claddings by 60% compared with the control trial. In the variant study, where the material investigated was used as a source of carbon, the butyl rubber layer was completely utilised. Degrading the glue layer of protective coating, bacteria affect adhesion to the metal, promoting its corrosion damage.<sup>20</sup>

Therefore, a biofilm, which is a community of bacteria and the products of their metabolism, is formed on the surface of coatings, which differ from each other by their chemical composition. Micro-organisms that form a biofilm are characterised by high metabolic activity and are capable of damaging the insulating coatings used for the protection of metals against corrosion.

Biodegradation of protective coatings is caused by the interaction of bacteria destructors with the deteriorating material. The obligatory condition for this process to occur is close contact of micro-organisms with the surface of the material, i.e. adhesion.

Adhesion of micro-organisms depends on a number of chemical, physical and biological factors, such as electrostatic interaction between bacteria cells and the surface of coatings, hydrophobic effect, various chemical (hydrogenous, amide and etheric) bonds, time of contact, as well as properties of the cell culture, including mobility, taxis, cell number, presence of exopolysaccharides or other adhesives.<sup>21</sup>

In the literature, there are few data on bacteria adhesion to insulation materials used for protection of underground structures against corrosion.

Cultures of bacteria isolated from corrosion sites on damaged oil bitumen and film coatings were investigated. A study of the influence of the time of bacteria contact with coating samples on bacterial adhesion showed that the maximum number of

bacterial cells adhere to the surface during the first 5 min. Thus, the share of *Ps. stutzeri* strain 22, which have adhered to polyethylene in the native culture during the first 5 min of exposure is 49% while, for a 60 min exposure, it is 33%. The highest share of cells which adhered to the surface during the first 5 min of exposure was observed on the surfaces of traditional bitumen materials BNI-IV and MBR-90 and amounted to 88 and 77%, respectively.

Much smaller numbers of adhered cells have been observed in the cases of polyethylene coating and bitumen coating modified by a corrosive inhibitor with biocide action, where these fractions vary from 10 to 26%.

In the opinion of Marshall,<sup>21</sup> adhesion of micro-organisms to a solid surface proceeds in two stages. During the first, inverse sorption stage, cells approach the surface and can even get into direct contact with it owing to attraction and repulsion forces. At this stage, micro-organisms can synthesise cell free polymeric materials which are required for irrevocable sorption characterised by strong bacterial adhesion to a surface. Micro-organisms are most frequently fixed to a surface by means of extracellular polymers.

Investigation of the adhesive capability of bacteria destructors of protective coatings is an integral part of fundamental research studies on the interaction of aggressive microbial colonies with industrial materials.

A biological factor controlling adhesion to solid surfaces is the slime producing ability of extracellular polymers. It is known that these slime compounds are mostly polysaccharides.

The cultures of the bacteria destructors investigated demonstrated a different ability for adhesion to coatings. Bacteria isolated from the damaged coatings were checked for slime producing ability, and 50% turned out to be capable of slime formation. In most cases, these were representatives of the *Pseudomonas* genus.

For further research on their adhesive capabilities, active slime forming cultures *Ps. stutzeri* strain 22 and *Pseudomonas* sp. 113 as well as cultures incapable of slime formation, *Pseudomonas* sp. strain 103, were selected. It was shown that the bacteria destructors investigated can synthesise exopolysaccharides.

A study of exopolysaccharides of *Pseudomonas* sp. strain 113 and *Ps. stutzeri* strain 22, which adhered to the investigated coatings, showed that they differ in their density of accumulation and monosaccharide structure. It was established that polysaccharides of *Ps. stutzeri* strain 22 contain ribose, xilose, arabinose and desoxyglucose.

**Table 4** Formation of hydrogen sulphide by *Desulfovibrio* sp. strain 10 in presence of protective coatings, mg L<sup>-1</sup> medium

| Experiment                                          | Exposition, days |       |       |        |       |
|-----------------------------------------------------|------------------|-------|-------|--------|-------|
|                                                     | 1                | 3     | 7     | 14     | 21    |
| <i>Desulfovibrio</i> sp. strain 10                  | 42.5             | 119.0 | 229.0 | 272.25 | 238.5 |
| <i>Desulfovibrio</i> sp. strain 10 + Polyken 980-25 | 46.75            | 55.25 | 178.5 | 255.0  | 195.5 |
| <i>Desulfovibrio</i> sp. strain 10 + Polyurethane   | 22.2             | 63.8  | 170.0 | 242.25 | 221.0 |
| <i>Desulfovibrio</i> sp. strain 10 + BNI-IV         | 38.25            | 127.5 | 238.0 | 272.25 | 221.0 |
| <i>Desulfovibrio</i> sp. strain 10 + BNI-IV, OK     | 12.75            | 42.5  | 89.25 | 106.0  | 102.0 |
| <i>Desulfovibrio</i> sp. strain 10 + BNI-IV, BLK    | 42.5             | 51.0  | 102.5 | 170.0  | 110.5 |

The structure of polysaccharides of *Pseudomonas* sp. strain 113 contains ribose, arabinose, xilose, galactose, desoxyglucose and inositol.

The composition of the polysaccharides investigated includes only aldoses, which provide high reactivity in these substances. The adhesion of bacteria to the surface of materials can be ensured not only by the rheological characteristics of the polymer, but also by the chemical interaction of aldehydic groups of polysaccharides with active groups on the coating surface.<sup>22</sup>

To determine other mechanisms of adhesion of bacteria to the surface of insulating materials, the hydrophobic and electrokinetic properties of cells of the cultures investigated were studied. Hydrophobic interaction between bacterial cell surfaces and other materials is an essential factor which promotes the adhesion of micro-organisms to these materials. These attraction forces link non-polar (hydrophobic) parts of molecules or complete molecules. The energy of separate interaction is insignificant, but a large number of such links can have a significant impact on the process of interaction of a molecule. Adhesion of the investigated bacteria to coatings depends not only on the properties of the cultures, but also on the surface of the materials investigated. The surface of bacteria, capable or incapable of slime formation, has hydrophobic sites.<sup>16</sup>

Results have shown that the highest parameter of hydrophoby (49.3%) is intrinsic to cells of *Pseudomonas* sp. strain 103, which did not form cell free slime, but demonstrated good adhesion to all the coatings studied (Table 5). The maximum share of adhered cells of this culture on the BNI-IV surface amounted to 56–75%.

Interaction of bodies with opposite electric charges promotes their attraction. The electrokinetic properties of bacterial cells are determined to a significant degree by the electrolyte content on their surface, which has amorphous properties, as well as by the functional condition of the bacteria, which stipulates the character of dependence of a surface electric charge on the pH value of the medium and its ionic structure. Owing to the quantitative prevalence of acid groups over alkaline, isoelectric points of bacterial cells are located in the field of low pH values whereas, in the case of their neutral values, the cell would have a negative electric charge.

Frequently, a negative charge is also characteristic of many solid materials. Despite the total negative charge of surfaces, the latter may contain separate sites which carry a positive charge and promote interactions between micro-organisms and insulating materials.<sup>17</sup>

During the assessment of values and signs of the electrokinetic potential of the cultures investigated, it

was established that bacterial cells have a negative surface electric charge (Table 3).

Therefore, adhesion of bacteria activators of corrosion to a surface of protective material can be caused not only by biological factors (exopolysaccharides), but also by physical and chemical factors, hydrophoby and electrokinetic potential.

The bacteria studied, which belong to the *Pseudomonas* genus, are adhered owing to the formation of exopolysaccharides. The extracted exopolysaccharides by their monosaccharide structure are active enough and can act as adhesive factors in relation to solid surfaces.

Some representatives of the bacterial community, which do not form slime, still have adhesive capabilities, but here the main adhesive factors are hydrophoby and a negative surface electric charge. These features promote the adhesion of cells to positively charged materials. adhesive capabilities, but here the main adhesive factors are hydrophoby and a negative surface.

Most adherent bacteria are observed on the surfaces of traditional bitumen coatings: BNI-IV and MBR-90. Reduction of bacterial adhesion is observed on bitumen which has been modified by a corrosive inhibitor with biocide action.

The coatings investigated can be rated by the degree of bacterial adhesion on their surfaces in the following sequence: oil bitumen, bitumen rubber mastic, polyethylene coating and bitumen modified by a corrosive inhibitor.

The efficiency of the corrosion protection of pipelines and other underground structures depends on the quality of passive protection, primarily the bioresistance of coatings. One of the causes of homogeneity failure and degrading of the protective properties of coatings is the vital activity of soil micro-organisms. There are limited references to the resistance of coatings to bacteria induced corrosion. The effect of antimicrobial modifying additives on the properties of oil bitumen lubricating coatings has received much less study.<sup>23</sup>

It is known that traditional oil bitumen coatings are more exposed to the action of micro-organisms than are film coatings containing components that can be used by bacteria as a trophic substrate.<sup>24,25</sup>

One way to improve the microbial resistance of coatings is to modify them with biocide substances which suppress the growth and replication of corrosion inducing micro-organisms.

Biocides such as spirits, phenols, oxidants (hydrogen peroxide, potassium hypermanganate, iodine, iodoform, hypochlorites, chlorine, chloramine), and salts of heavy metals (copper, mercury, silver) are chemicals which act as destroyers of various micro-organisms. These substances coagulate proteins, oxidise sulphohydryl groups in protein structures and thus destroy micro-organism cells.

On average, only one in 4000 compounds studied as potential biocides could be applied in practice.<sup>26</sup> In the laboratory, it is found that, in contrast to standard cultures, 'wild' types of micro-organisms are more aggressive with respect to the materials tested. The assessment of biocide efficiency determines its effect on micro-organism cells embedded in film as a bacteria population.

**Table 5 Hydrophobic and electrokinetic potential of heterotrophic bacteria**

| Bacterial culture                 | Hydrophoby, % | Electrokinetic potential $\xi$ , MV |
|-----------------------------------|---------------|-------------------------------------|
| <i>Ps. stutzeri</i> strain 22     | 25.5          | –30.5                               |
| <i>Pseudomonas</i> sp. strain 113 | 32.7          | –36.5                               |
| <i>Pseudomonas</i> sp. strain 103 | 49.3          | –30.5                               |

Analysis of the data obtained revealed that, for 30 materials studied, bactericide properties were found for katizol and its composites. In the presence of oil bitumen BNI-IV, the population of DNB and HCOB increased by 20–40% in relation to the control (media + bacteria) level. In test experiments where the surface was the only source of carbon, the growth of bacteria was observed on the whole surface of the samples investigated. Bitumen rubber mastic MBR-90 was almost inert in its effect on DNB and HCOB. BNI-IV modifications by shale oil products, BLK, OK, SF, MKS, suppressed HCOB and DNB. MBR-90 composites with KHO-1–KHO-4 inhibitors were bactericide to SRB and TB. This is in line with Pilyashenko-Novokhatny's finding<sup>27</sup> as to complete KHO inhibitor induced suppression of sulphate bacteria corrosion and enzymatic activity. Modification with MKS, KO SZhK and their compositions of BNI-IV suppressed the vital activity of TB by 40–60%. As to the effect on SRB, BNI-IV, MD were more active.

The corrosion inhibitors studied, biocides, suppress the vital functions of corrosion inducing bacteria that could be attributed to absorption of these substances on the cell surface and irregularity of cell metabolism. It is important to note that they suppress denitrification and sulphate reduction processes which are responsible for the production of corrosive active metabolites ( $\text{NO}_2^-$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ), which in turn leads to the reduction of environment aggressiveness. The data obtained are also of great interest because the DNB, the main functions of which are suppressed by the inhibitors mentioned, are not only degrading agents on protective coatings but also cause metal corrosion. Degradation caused by these microorganisms could be compared with the corrosive activity of SRB,<sup>28</sup> though there is little evidence of a role of DNB in metal corrosion to date.<sup>29,30</sup> The data obtained for the effect of these reagents on the basic function of bacteria inducing degradation will assist targeted research of biocide corrosion inhibitors.

## CONCLUSIONS

The reliability of metal underground structures depends first on the state of the corrosion preventive protection which is carried out by means of insulating coatings. One of the causes of deterioration in the protective properties of materials is the life activity of bacteria in soils, which can initiate or promote corrosion processes.

The application of 'bioresistance' as a material quality indicator can provide rapid assessment of the deterioration rate of coatings and predict their resistance to microbial destruction in a particular environment.

The efficient alternative to improving the bioresistance of bitumen coatings is their modification by commercial products of carbon and shale resin processing (KHO series of corrosion inhibitors): road oil, shale fraction and kukersite base. The application of these modifiers does not degrade the physical and mechanical properties of coatings. In the development

of corrosion protection insulation of pipelines and processes for the coating industry, it is necessary to take into account the selective action of modifiers and coating-modifier systems on corrosion inducing bacteria. Therefore, the coating formula requires adjustment, depending on the soil biocorrosion activity in a particular region.

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