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# Comprehensive Analysis of Electrochemical and Structural-Dynamic Properties of Bitumnious Insulating Materials

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## Abstract

At the current stage the strategic trend of development of the oil and gas industry is increase in the oil conversation depth with the use of relatively new approaches and methods of mining, treatment, transporting and processing of different kinds of hydrocarbons. Along with that, implementation of new processing techniques, improvement of the production performance and quality of the output products, intensification and reconstruction of the existing oil and gas plants depend not only on the structural materials used but also on the right choice of anti-corrosive materials for protection thereof. According to the existing ideas of the most important factors determining anti-corrosive properties of bituminous insulating materials is mechanical insulation of the material from the aggressive media. Since the insulating film consists of the areas of different density with numerous micropores then by the coating contact with water or electrolyte solutions liquid penetration through the film (diffusion) as well as moisture adsorption by active centers of the film binder (swelling) take place. The criterion of insulating capacity is high effective resistance (minor permeability), low capacity (minor swelling) and slow change in the behavior in the time domain[1-3]. No less important factor determining the protective action of coatings is film adhesion ensuring not only film adhesion to the material but also preventing appearance of a new phase on the at the metal-film border. The film adhesion strength is affected by the internal stresses arising during the process of coating formation and relaxation processes. In order to protect material from corrosion, special substances are introduced in the insulating material that is able either to change kinetics of electrode reactions determining the corrosive process or inhibit it.

**Keywords:** Bitumen, Composition, Composite Protective Material, Coatings, Electrochemistry, Oil and Gas Equipment, Physical-Mechanical Properties

## 1. Introduction

Most of materials applied in the industry and equipment, devices made of them are unstable in the environment, i.e., is subjected to corrosion. Extension of their life time will allow saving millions tons of metal, reducing the production costs. Metal structural materials are especially susceptible to destruction. Acuteness of this problem is felt in all developed countries as the rate of growth of corrosion losses exceeds the rate of growth of metal production being the main strategic structural material in the oil and gas producing, chemical and refining industrial complex of the Russian Federation. During the process of operation the metal parts under exposure of various factors are subjected to corrosion damage due to the fact that metal seeks transition to a bound state - that is thermodynamically more favorable under normal conditions. This results in significant financial loss, reduction of the equipment reliability and reduction of the total metal stock. According to the estimates of foreign experts, the damage from corrosion in the economy of developed countries makes 3-3, 5% of the gross national product

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amount. Even though as of today this issue is far from being completely resolved, the accumulated experience allows specifying the main trends in fighting against corrosion: the use of corrosion-resistant steels and structural materials, cathode protection, use of protective insulating and/or plastic materials, combined methods. According to the Central Scientific-Research Institute project steel structure, the national industry satisfies the construction demand for anti-corrosive materials at 60% only and is behind the foreign ones by many specifications: ecological cleanness, processibility, drying period, color palette. One of the most efficient methods in fighting against corrosion is application of insulating materials on the basis of modified oil bitumen - this is the method of durable anti-corrosion protection on the basis of high-molecular film-forming substances with additions of corrosion inhibitors and solvents. An important component of the protective action of bituminous film is inhibition of the process of penetration of the corrosion active medium in the substrate surface. Within this context hydrophobic properties and water-resistance refer to characteristics enabling metal corrosion prevention. This determined the topicality of design of Bituminous Insulating Materials (BIM) distinguishing through high insulating properties in respect of water media[2-6], the rate of water diffusion into bitumen makes 0,4 0,8•10-8 g/(cm•h•mm Hg), i.e. 0,83•10-15 1,66•10-15 kg•m/(sec•n) and is determined by low solubility of water in bitumen, water adsorption by bitumen depends on its hardness, by contacting moisture vapor it makes 0,001…0,01 percent and by lasting keeping of bitumen in water does not exceed 1÷3 percent, water conductivity of bitumen is much lower than that of rubber and many plastic materials. The cheapness and domestic raw materials base are additional advantages of bitumen as the film-forming basis. However, it shall be noted that high rates of growth of the oil industry resulted in quick depletion of high-rate reservoirs that are currently depleted by 89% and the share of difficult reserves increased from 33 to 66%. One of the issues is development of the large oil reservoirs by more than 90 percent[3].

Natural bitumen is to a different extent oxidized high-viscosity oils of liquid, semi-liquid and hard texture with high content of sulfur, resins and asphaltenes. In contrast to oil, they are characterized by increased content of vanadium, nickel, molybdenum and significantly smaller content of gasoline and diesel fractions. In light of this, design of the intensive technology of refining of High-Viscosity Oils and Natural Bitumen (HVO and NB) Black Oil (BO) with account for the scientific accomplishment of the physical-chemical mechanics of Oil Disperse Systems (ODS) for the purpose of production on the basis thereof of the new demanded composite materials with the specified properties is a topical task. Along with that, due to the specific properties – strength, thermal plasticity, water-resistance, resistance to action of weather factors and aggressive media, slight electrical and heat conductivity, etc., natural bitumens just like artificial ones may find application as anti-corrosive coatings, electrical insulating materials, radiation shielding, construction of asphaltic barriers for water retention on soils, etc. This is why, despite the steady increases in production of synthetic resins, bitumens are still used as affordable film-formers for anti-corrosion protection. The low physical-mechanical, namely, hardness, adhesion and strength are the factors constraining wide use of coating on the basis of bitumen. This is related to the peculiar features of the chemical composition of the raw material, namely, high content of long-chain paraffin Hydrocarbons (HC), technological conditions of black oil refining. Today in Russia the high-quality meeting the GOST 21822-87 requirements are produced from the highly-resinous low-paraffin oil from the Yarega deposit. This fact significantly constrains the possibility of increase in the bitumen production for BIM output while the demand is increased and the area of application is enhanced. It shall be emphasized that the special high-melting point asphalt as a BIM component beside compliance with the GOST 21822-87 shall ultimately ensure optimal adhesion and strength characteristics of the coating, the values of which shall fall within the range from 1 to 2 points and mm, accordingly, and the hardness – within the range of 0,067 - 0,2 conventional units and higher.

For the most part, there is no principal correlation between the existing methods of oil and natural bitumen production, conditions of further processing and the quality requirements set by the consumers of the modern market for insulating materials, so the task of production of high-quality BIM becomes difficult and often impossible to fulfill due to the high growth of negative factors related to the effect of the chemical-structural-group composition of destructive BO and bitumens on the adhesion-strength properties of BIM produced on the basis thereof. The solution to the situation established is selection of Polyfunctional Modifiers (PFM) featuring high self-curing capacity on different kinds of supports, along with that strict adherence of conditions, namely – the material designed shall feature high insulating capacity, necessary set of adhesion-strength and stress-strain properties under different conditions of application - is required[5-12]. Accordingly, in order to improve the insulating capability of bitumens of regional origin and materials on the basis thereof it is needed to perform targeted selection of modifying additives of structuring kind (thermosetting materials)[13,14]. At the same time the task of complete compatibility of additives with the bitumen compositions with different chemical composition arises. For this purpose the detailed selection of component of synthetized modifiers shall be performed so that each of them features sufficient thermal stability as well as high degree of physical-chemical compatibility that can be characterized on the basis of solubility laws[13,14].

According to the existing ideas of the most important factors determining anti-corrosive properties of bituminous insulating materials is mechanical insulation of the material from the aggressive media. Since the insulating film consists of the areas of different density with numerous micropores then by the coating contact with water or electrolyte solutions liquid penetration through the film (diffusion) as well as moisture adsorption by active centers of the film binder (swelling) take place. The criterion of insulating capacity is high effective resistance (minor permeability), low capacity (minor swelling) and slow change in the behavior in the time domain[1-3]. No less important factor determining the protective action of coatings is film adhesion ensuring not only film adhesion to the material but also preventing appearance of a new phase on the at the metal-film border. The film adhesion strength is affected by the internal stresses arising during the process of coating formation and relaxation processes. In order to protect material from corrosion special substances are introduced in the insulating materials that are able either to change kinetics of electrode reactions determining the corrosive process or inhibit it. The criterion of insulating capacity is high effective resistance (minor permeability), low capacity (minor swelling) and slow change in the behavior in the time domain[14]. No less important factor determining the protective action of coatings is film adhesion ensuring not only film adhesion to the material but also preventing appearance of a new phase on the at the metal-film border. The film adhesion strength is affected by the internal stresses arising during the process of coating formation and relaxation processes. In order to protect material from corrosion special substances are introduced in the insulating materials that are able either to change kinetics of electrode reactions determining the corrosive process or inhibit it. Such substances are primarily micro-ionized fillers containing $Cr^{3+}$, $Cu^{2+}$, $Fe^{3+}$ and featuring complexing action, i.e. increased adhesion is determined by inclusion of functional groups of the film former and hydroxyl groups of metal substrate in the internal sphere of the complex, i.e. formation of coordination bonds between the film-former molecules and the metal surface. It is thought that such fillers exert catalyzing effect on the spatial transformation of film-formers. This takes place when filler or the product with its interaction with components of the film-forming system is the catalyst of the spatial cross-linking process. Such effects take place in the film-formers when they are filled with oxides of metals of mixed valence. Stable bond of the binder and particles of disaggregated filler as well as between the film and substrate is one of the key requirements imposed on the paint suspension and the film being formed. The role of film-forming substances in the protective coating action shall be considered not only in terms of their chemical composition but also in terms of mutual impact of all the system components (binder, filler, solvent, plasticizer, hardener). It shall be noted that Thermal-Polymeric Resins (TPR) featuring higher level of affinity to the filler surface as compared to the bitumen components are concentrated in the form of adsorption layer on the surface of filling particles. TPR fulfills the role of promoter of filler-binder adhesion in the coating facilitating efficient transfer of stresses arising in the film from the organic matrix to high-modular filler.

Performance of electro-chemical analysis of the filled BIM speaks of high protective capacity to the processes of cathode polarization of electro-chemical process which is presented in the Figures 1-4.

Above the results of electro-chemical analysis are presented among which special attention was paid to galvanostatic method of estimation of penetration of electrolytic solution ions through the layer of the filled BIM towards the metal substrate surface shown in Figure 2 and Figure 3. The peculiar feature of it is that the value set is current density and potential that is constant in time is recorded. It shall be noted that here and elsewhere in the electro-chemical experiments performed the corrosion process was investigated with the use of cathode control shown in Figure 4.

In the accelerated tests of electro-chemical process in BIM the cathodic reaction of metal ionization does not prevail over the anodic one, thus, kind of passivation is

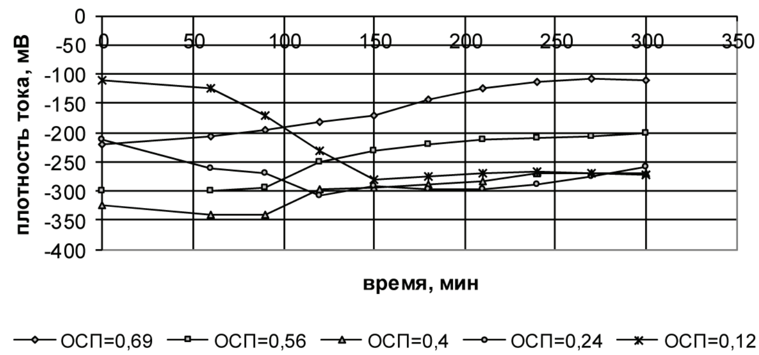


**Figure 1.** Electro-chemical analysis of the filled BIM modified DST at different OSB in course of time (holding time 3 days).

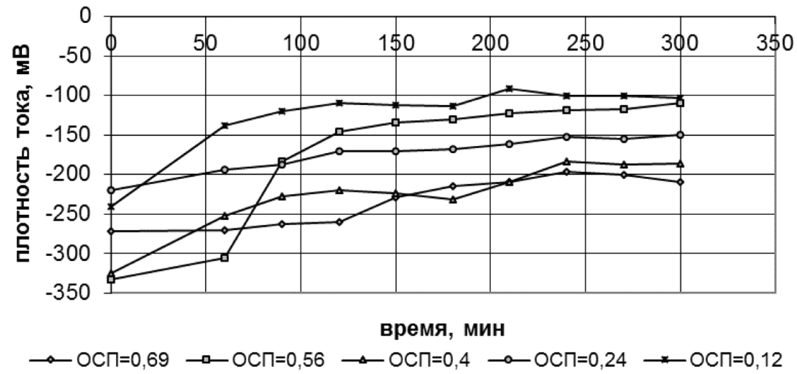


**Figure 2.** Electro-chemical analysis of the filled BIM modified DST at different OSB in course of time (holding time 7 days).

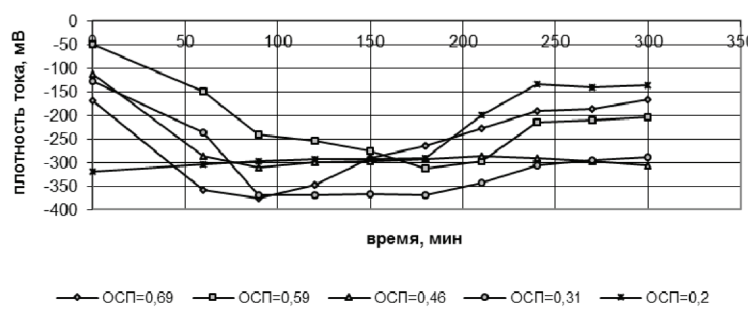


**Figure 3.** Electro-chemical analysis of the filled BIM modified LMS at different OSB in course of time (holding time 3 days).

observed. The current density values lie within the negative domain which does not result in increase in the corrosion rate. The introduced inhibited systems containing DST and LMS components are not oxidizers which often promotes to oxy-polymerizing reaction behavior, thus. According to the performed comprehensive analysis of the filled BIM it may be concluded that the optimal filling is OSB equal to 0,4 in coatings containing DST; and OSB equal to 0,46 in coatings with LMS. By comparing coatings of different polymers we distinguish coatings with the use of the inhibited polymer LMS as their physical-chemical and insulating properties are

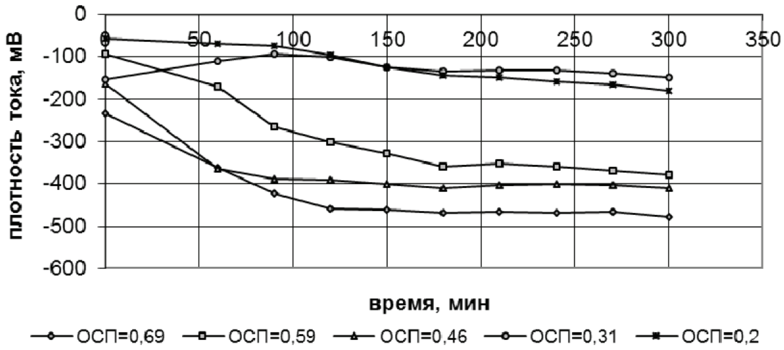


**Figure 4.** Electro-chemical analysis of the filled BIM modified LMS at different OSB in course of time (holding time 7 days).

**Table 1.** Structural-dynamic analysis of components

| Name | Number of acc. | Number of 180 | Step seq.. ms | Delay time, ms | Amplitude | $T_2$, ms | P,% |
|---|---|---|---|---|---|---|---|
| Filler IM 2201 | 5 | 180 | 550 | 650 | 3,21 | 3,02 | 100 |
| xylene | 10 | 300 | 2500 | 500 | 94,17 | 645 | 100 |
| TPR - xylene | 10 | 500 | 1800 | 265 | 334,58 | 344 | 100 |
| TPR– LMS - xylene | 10 | 260 | 1900 | 1100 | 125,90<br>1140,51 | 393<br>15,9 | 10<br>90 |
| TPS – DST - xylene | 10 | 350 | 1500 | 2500 | 144 | 413 | 100 |

a sequence higher than those of coatings with the use of the DST polymer, we'd also like to note that LMS is production waste this is why the cost of such coating will be lower.

Structural-dynamic analysis of components of the filled BIM. Table 1 presents the structural-dynamic analysis of components of the filled BIM.

## 2. Conclusions

According to the structural-dynamic characteristics it may be concluded that the system xylene – TPR is single-phased as the value of proton population is taken for 100%. This fact completely sustains the theory of intersolubility of different components by Hildebrandt. Along with this, thermo-dynamic equilibrium is rapidly changed by combining with the solution xylene – TPR – low-molecular SEV the composition of which as was suggested contains high-molecular inclusions characterized within the ranges of NMR-relaxometry by high amplitude values – 1140,51 and low time of spin-spin relaxation – 15,9 msec. The changes taking place in a polymeric system by introduction of LMS into its composition are related primarily to the diffusion processes LMS, NPS within the xylene medium as well as to the competing role of LMS in the processes of structuring of the disperse medium through execution of the LMS solving process through swelling thereof which may be somewhat constrained. This is explained by the fact that solvent capacity of xylene under normal conditions ($20^0$C) is reduced due to high solubility within the TPR arene.

## 3. Summary

Adhesion capacity of inhibited polymeric systems of the basis of LMS and ТПС is related to the fact that their composition contains up to 90% wt of slow-moving segments of polymeric chains facilitating intensive execution of the structure-forming processes within different media, in the elementary cell of the molecular skeleton of which, for example, Complex Structural Units (CSU) of tars and bitumens will be located. This will promote both to increase in the system stiffness in whole and to increase in the coating hardness and acquisition or maintenance of thixotropic properties in BIM. Comparative analysis of polymeric systems with the use of LMS and DST confirms reasonability of choosing DST as the polymeric system base. This is proved by the single-phase condition of the polymeric system. The changes observed are explained by the chemical composition of polymeric fillers being combined, namely – divinylic and styrene as well as high degree of TPR unsaturation within an individual aromatic solvent. This is why by combination with high-melting point bitumen high level of electrochemical resistance to ion penetration is observed.

## 4. Conflict of Interests

The author confirms that the data provided does not contain the conflict of interests.

## 5. Acknowledgments

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