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TECHNOLOGY FOR ANTICORROSIVE PROTECTION OF STEEL STRUCTURES BY COATINGS BASED ON RAPID-SETTING BITUMEN-LATEX EMULSION

Mix formulas for rapid-setting bitumen-latex emulsions and coatings based on them have been designed; in-laboratory tests of their physical, chemical, and anticorrosive properties have been carried out. The technology for anticorrosive protection and the technical documents for preparing the aqueous bitumen-latex emulsion have been designed; a plant has been mounted and a pilot batch of rapid-setting emulsion has been produced. The technology has applied to pipelines in the oil and gas industry.

Keywords: bitumen-latex aqueous emulsion, emulsifier, initiator, inhibitor, anticorrosive coating, and adhesion.

Recently, in Ukraine, the necessity for designing advanced, efficient, simple, reliable, and environment friendly insulating coatings for protection of metallic structures from corrosion has become very evident. This problem is especially important for anticorrosive protection of pipelines, oil tanks, various machinery, etc. [1]. Among the ways to solve it, there is the use of coatings based on rapid-setting (RS) bitumen emulsions (BE). There is a set of modified BE containing different admixtures: derivatives of monocarboxylic acids, biolipid extracts, epoxy fat acids, sodium salts of carboxymethyl cellulose and phosphorous acids, natural latex, liquid rubber, homopolymer of acrylamide and so on.

The conventional technique of coating with hot bituminous mastics is low-tech, power intensive, and environment unfriendly. In addition, in this technology, the formation of anticorrosive coating can cause strain aging of metal which previously has undergone plastic deformation (especially, in the case of pipelines). As a result, before the start of operation, the metal resistance to brittle rupture significantly decreases.

The majority of advanced economies have abandoned out-of-date techniques for bitumen dilution (with organic solvents) or heating to melting point. The widespread method there is cold preparation of BE having a significantly lower viscosity, comparable to that of aqueous phase, at a temperature of 20 °C and a higher adhesion to the surfaces of different structure and nature. The foreign experience shows [2] that the cold technologies with the use of BE in road construction enable bitumen saving by 30% and almost 1.5 time reduction of power consumption. Therefore, in the view of improving binder properties, reducing power consumption and harmful emissions to environment, raising efficiency and safety of works, the share of polymer modified BE is expected to grow in the near future. The latexes are promising bitumen modifiers for obtaining PMB composite materials having a wide range of properties and backed by sufficient raw material base [3].

The Karpenko Physical and Mechanical Institute of the NAS of Ukraine has designed and tested MF of bitumen-latex aqueous emulsions [4, 5] and coatings based on them, studied the physical, mechanical, and anticorrosive properties. *Techno Resource* Engineering Center of the NAS of Ukraine deals with commercialization of this R&D product.

The technique foresees the two main stages: *1)* synthesis of bitumen-latex aqueous emulsion and *2)* formation of rapid-setting coating during its cold application to metallic surface due to special admixture (initiator). The second stage includes instant water displacement to surface of the coating, which opens up prospects for application of this coating to the wet surface.

PREPARATION OF AQUEOUS BITUMEN EMULSION

The content of main components in BE may fluctuate within a wide range: petroleum bitumen 40—80%; emulsifiers 0.5—3.0%; stabilizers 1—3%. The anion BE (Nynas bitumen 100/150—60%; emulsifier (Redicote 505)—1.1%; stabilizer NaOH; water) was chosen as basic composition. The physical and chemical parameters of the composition complies with requirements of DSTU B V 2.7-129-2006 (Table 1, column 3).

BITUMEN EMULSION MODIFICATION

The emulsion was modified by *TOPTEX B* latex of styrene-butadiene synthetic rubber (SBR-polymer) (Fig. 1), a thermo-elastic polymer getting hard while dewatering. It acts as polymeric matrix where bitumen drops are located. The styrene-butadiene molecular structure enables building a polymeric matrix that ensures combinations of important properties such as, strength and elasticity. At the same time, bitumen, as filler, forms required adhesion of material and resistance to impact.

At concentrations 3, 5, 7, 10 and 15 weight % of BE, latex does not change appearance of mix, its homogeneity, and stability during storage. Therefore, as admixture, in the above quantity, it does not influence the service life. As latex concentration a grows, so does the content of solid phase c in the composition (Fig. 2), since its content in styrene-butadiene latex is slightly higher as compared with primary BE: 64.0 ± 1.0% versus 60.2%. Low latex concentration (a = 3—7%) has been estab-

Table 1

Physical and Chemical Properties of Anion Bitumen Emulsions: Nonmodified (EA) and Modified (EAM)

Parameter	Requirements DSTU B.V 2.7-129-2006	% of latex			
		0	3	5	7
Appearance	Dark brown liquid without coagulated bitumen	matches	matches	matches	matches
Conventional viscosity, c, max	20	12.2	12.0	11.7	7.8
Homogeneity (sieve residue № 014), %, max	0.5	0.01	0.01	0.01	0.01
Hydrogen ion concentration, *pH*	8—12	10.3	9.6	9.38	9.15
Solid phase content, %	50—70	60.2	60.3	60.6	61.3
Stability: (sieve residue № 014), %, max:					
after 7 days	0.8	0.01	0.01	0.01	0.05
after 14 days	1.2	0.01	0.01	0.01	0.05

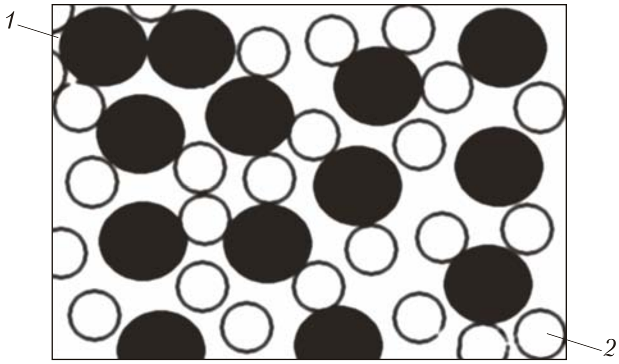

Fig. 1. Latex-bitumen composite: *1* — latex; *2* — bitumen

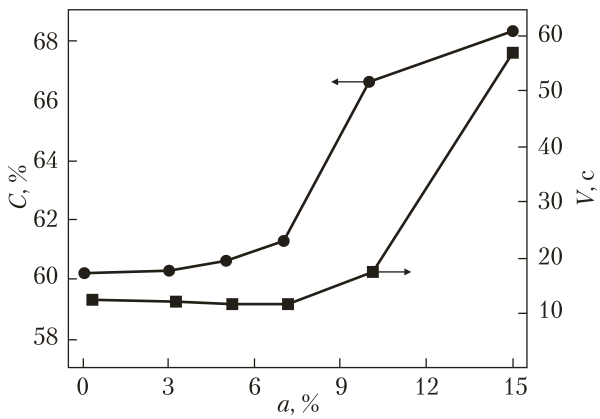

Fig. 2. Dependence of solid phase content (curve 1) and relative viscosity (curve 2) of BPC on concentration of *a* styrene-butadiene latex

Fig. 3. 325 mm diameter pipe coated with BPC

lished practically not to change viscosity of composition *v*, however, at high concentration *a* (10—15%) it increases materially.

It should be noted that, within the range of concentration under review, the latex content almost does not influence the other properties of modified BE (see Table 1).

FORMATION OF BPC COATING

The BPC coating on the metal surface is formed under the influence of *initiator*, a inorganic compound capable of ruining the shells of micelles created by emulsifier. While agglomerating, the fine dispersed particles of polymer create a sort of membrane on the metallic surface, with bitumen drops residing in the membrane hollows. The time of formation of this coating is 1—5 s. After dewatering, the coating gets anticorrosive properties.

It should be noted that the coating has continuous even surface with homogeneous distribution of material, without any bumps or flaws. The BP coating gets stabilized in ~24 hours after application (it does not change the shape under the pressure, with no traces remaining on its surface).

The main properties of the coating depending on latex concentration in bituminous emulsion are given in Table 2. Some parameters change significantly only at high concentration a. For example, at maximum concentration *a* = 15%, the softening and melting points of the composition grow by 9—12° on the average, whereas the dielectric continuity increases by 10 kV/mm as compared with the 3% latex composition. However, as a whole, the properties obtained comply with the requirements for coatings of this type.

On the basis of test results, with structural specificity of protective coatings of this type taken into consideration, in order to get a reliable integral structure of the coating, 5—7% latex composition was selected as optimal BPC. Table 3 shows the general properties of *primer—coating—strip* system in terms of anticorrosive protection of pipelines (Fig. 3).

The obtained data comply with requirements of DSTU-4219-2003, with several ones (dielectric continuity and resistance to impact) exceeding them.

INHIBITOR EFFECT ON PHYSICAL, MECHANICAL, AND ANTICORROSIVE PROPERTIES OF BITUMEN-LATEX COATINGS

As mentioned, the specific feature of bitumen-latex emulsion setting is water displacement to surface. However, its finely dispersed drops can be left in the pores thereby impairing the anticorrosive properties. To enhance the protective properties of the primers, the lacquer coatings [6], and, in some cases, the bituminous ones [7, 8], inorganic, organic, and diphilic inhibitors are added to composites. The inorganic inhibitors that neither impair demulsifying action of initiator nor influence setting time (sodium nitrate (inhibitor 1) and sodium tungstate (inhibitor 2) as well as their organic derivatives known as steel corrosion inhibitors in neutral and low-acid environments were chosen for the present research [9]. Being gradually dissolved in water they protect metal that is in contact with coating pores.

The anticorrosive properties of coatings have been estimated by changes in the steel coated surface condition after exposure in a chamber, in the salt mist (3% NaCl), at a humidity of 90% and a temperature of 30 °C [8]. For the purpose of control, the samples were taken out after 4; 10; 24, and 39 days of exposure. The following parameters were estimated: visual condition of the coating (color, flaws, peeling); adhesion; after complete removal of coating the condition of metallic surface (time of appearance and number of pits, spots, rust, etc.).

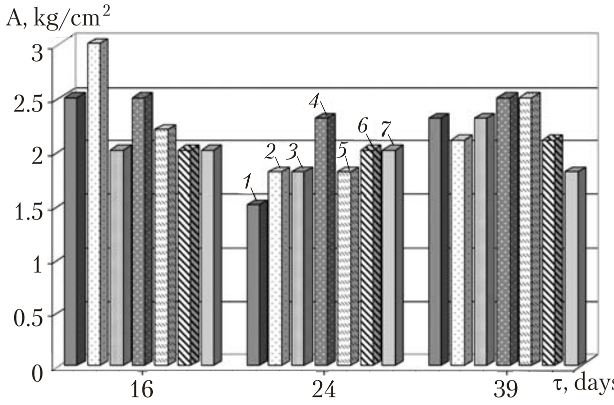

Fig. 4. Effect of time of exposure in hydraulic chamber τ on adhesion *A* depending on inhibitor concentration in the coating: *1* — inhibitor-free; *2*, *5* — 0,1 g/l (inhibitors Inh 1 and Inh 2, respectively); *3*, *6* — 0.2 g/l; *4*, *7* — 0,4 g/l

Table 2

Coating Properties Depending on Latex Concentration in Emulsion Composition

Parameter	Concentration *a*, weight. %				
	3	5	7	10	15
Total thickness of coating, mm	0.58	1.02	0.63	0.27	0.74
Softening point, °C	57	46	55	55	66
Melting point, °C	73	70	72	78	85
Dielectric continuity, kV/mm of thickness	5	5	5	12	15
Adhesion to steel, Pa	1.9	2.9	1.8	1.0	1.7

Table 3

***Primer–Coating–Strip* Properties**

Parameter	Requirements of DSTU 4219-2003	Test results
Total thickness of coating, mm, at least:	2.0	2.2
Primer		0.06
Coating (*a* = 5%)		0.94
2 layers of strip		1.2 (0.6 × 2)
Dielectric continuity	No electric breakdown at a voltage of 5 kV/mm	The coating endures an voltage breakdown at 20 kV/mm
Resistance to impact, J, at least	8.0	15.0
Adhesion of strip to material, kg/cm²	—	0.5

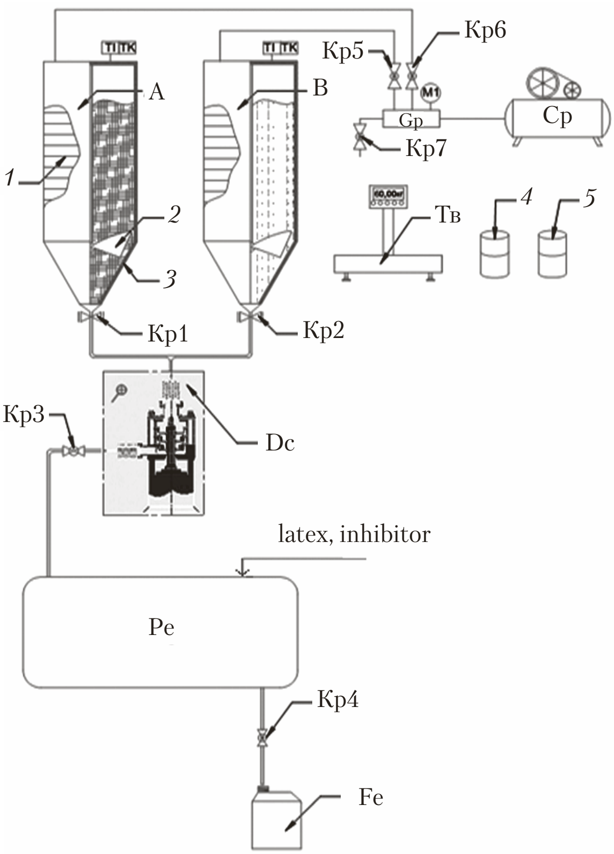

Fig. 5. Flow chart of BLE plant: A — smelt mill; B — mixer for preparing alkaline aqueous emulsifier solution; *1* — electric heating bundles; *2* — electric mixer; *3* — heat insulation; *4* — latex container; *5* — emulsifier and alkali container; 6 — electric mixer; Dc — high-speed (3000 rpm) dispenser; Kp1 and Kp2 — disc valves; Kp3—Kp7 — ball valves; Cp — air compressor; Gp — air manifold; M1 — manometer; $T_в$ — strain-gauge balance; Pe — mixer for preparing BLE; Fe — can for packing ready emulsion

Within the concentration range studied (0.1—0.4 g/l), the inhibitors have been established almost not to influence penetration [10], and, therefore, thermal resistance of the coating (Table 4). It should be noted that the penetration of the bitumen-latex coatings is materially lower as compared with the petroleum bitumen used in road industry (4.0 mm), which makes these coatings advantageous.

The inhibitors neither effect the structuring of coatings nor shift the softening point (Table 4) that ranges within 55—57 °C. It should be noted, that the exposure in the chamber does not change thermal resistance of both background and inhibited coatings, which means the stability of their physical and mechanical properties within the limits of parameters studied.

An important factor showing the effectiveness and reliability of the coating is its ability to keep the anticorrosive properties under high temperature and humidity and increased time of action of these factors. The tests in the chamber have showed that an increase in the time of exposure of the samples under given conditions leads to insubstantial impairment of their protective properties as single bumps of various size arrear. After 39 days, on the uninhibited coating, one can find some merged bumps where the surface under coating features some pits. After complete removal of coatings and cleaning of metallic surface, it has been established that during the first 4—10 days of exposure in salt mist, the steel under uninhibited coating almost does not bear pits. Further, as time goes by, the number of pits increases.

Table 4

Inhibitor Concentration Effect on Penetration (mm, temperature 25 °C, load 50 g during 5 s) and Softening Point (*t*, °C) of Bitumen-Latex Coatings Before and After Exposure in the Chamber

Parameter	Without inhibitor	Inhibitor № 1			Inhibitor № 2		
		concentration, g/l					
		0.1	0.2	0.4	0.1	0.2	0.4
Penetration, 0.1 mm, 25 °C	7.4	7.3	7.6	7.5	7.2	7.4	71
t, °C, 24 hours before exposure	55	55	55	57	56	57	57
t, °C, 24 hours after exposure	55	55	55	57	56	56	57

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In the presence of inhibitors, the formation of bumps and pits on the coating substantially slows down. At a sodium nitrate concentration of 0.4 g/l, after 10—24 days of exposure, single bumps might appear on the coating, however, the substrate does not feature corrosive manifestations. Extension of exposure time up to 39 days has almost no effect on the coating and does not cause pit appearance. At the same concentration, sodium tungstate (inhibitor 2) has showed a much better protective effect, as during the whole duration of the test, the coating remains shining and the steel does not suffer from local corrosion.

As a result of the tests, no clear dependence of coating adhesion to steel on inhibitor concentration has not been recorded as the adhesion ranges within 1.5—3 kg/cm^2. Within the studied time range, the lowest adhesion for both the reference and the inhibited samples was reported on the 24th day of test (Fig. 4). This coincides with visual observations of bump formation on the coating: after 24 days of test, the number of bumps increases materially, but further, as the test continues, they disappear.

Hence, addition of 0.4 g/l sodium tungstate as inhibitor to RS bitumen-latex emulsion significantly enhances anticorrosive properties of the coating and stabilizes its physical and chemical properties.

Fig. 6. The plant for preparing BLE

COMMERCIALIZATION OF R&D WORKS

The ultimate product of R&D works is the above described technology for production of bitumen-latex emulsion and a pilot shop for its application. The technology has advantages over the conventional methods (Table 5) due to reduced consumption of binder (by 20—40%), power consumption (by 40%), and mitigated environment risks.

Table 5

Advantages of Coatings Based on RS Bitumen-Latex Emulsion as Compared with Conventional Bituminous Coatings

No.	Main parameters	Conventional bitumen	RS coating
1	Type of insulation	Basic and field	Basic and field
2	Necessity of heating during application	Up to 160–180 °C	no
3	Necessity of heating during transportation	Up to 160–180 °C	no
4	Time of formation of layer	10—30 min	Several seconds
5	Light organic substances evaporating during application	Yes	no
6	Smoke black and fume	Yes	no
7	Ignition risk	Yes	no

CONCLUSIONS

The technology applies primarily to oil and gas facilities. The pilot plant for mixing RS bitumen-latex emulsion (Figs. 5, 6) has been designed and tested, and pilot batch has been produced in collaboration with *Pulsar&Co* Ltd. (Rivne) and *Naftogazbud*; the technology has been tested under industrial conditions (applied to a 325 mm diameter pipe). The anticorrosive coating having a total thickness of 3.0 mm is structured in accordance with TU U 23.9-03534506-003-14 and consists of the following layers: BP primer; emulsion; reinforcing material manufactured by *Pulsar&Co* Ltd.; emulsion; PVC film; and cover manufactured by Odesa Factory of Decorating Materials. The coating has been certified as the one complying with requirements of DSTU 4219-2003.

The technology can apply to insulation works (*Ukrtransnafta, Ukrtransgaz, Ukrgazvydobuvannia, Naftogazbud, Naftogazbudizoliatsia, Techno-Resource*, Center for Advanced Technologies for Road Construction and Rehabilitation, Ltd) and manufacture of insulation materials (Odesa Factory for Decorative Materials, Ukrainian Center for Radiation Technologies, *Diver* Ltd, *Pulsar&Co* Ltd). It is promising for the application in other industries as well, since it ensures high-quality, reliable, and cheap anticorrosive protection of steel structures.

The research is implemented within the framework of R&D project of the NAS of Ukraine «Development of Technology for Anticorrosive Protection of Pipelines and Steel Structures Using the Coatings Based on RS Bitumen-Latex Emulsion» (2014), reg. no.0114U000924.

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ТЕХНОЛОГІЯ ПРОТИКОРОЗІЙНОГО ЗАХИСТУ СТАЛЕВИХ КОНСТРУКЦІЙ ПОКРИТТЯМИ НА ОСНОВІ ШВИДКОТВЕРДНОЇ БІТУМНО-ЛАТЕКСНОЇ ЕМУЛЬСІЇ

Створено рецептури швидкотвердних бітумно-латексних емульсій і покриттів на їх основі, проведено лабораторні випробування їх фізико-хімічних та протикорозійних властивостей. Розроблено технологію протикорозійного захисту, технічну документацію на установку для отримання водних бітумно-латексних емульсій, змонтовано установку та випущено дослідну партію швидкотвердної емульсії. Проведено дослідно-промислову перевірку технології нанесення покриттів на труби нафтогазової промисловості.

Ключові слова: бітумно-латексна водна емульсія, емульгатор, ініціатор, інгібітор, протикорозійне покриття, адгезія.

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ТЕХНОЛОГИЯ ПРОТИВОКОРРОЗИОННОЙ ЗАЩИТЫ СТАЛЬНЫХ КОНСТРУКЦИЙ ПОКРЫТИЯМИ НА ОСНОВЕ БЫСТРОТВЕРДЕЮЩЕЙ БИТУМНО-ЛАТЕКСНОЙ ЭМУЛЬСИИ

Созданы рецептуры быстротвердеющих битумно-латексных эмульсий и покрытий на их основе, проведены лабораторные испытания их физико-химических и противокоррозионных свойств. Разработана технология противокоррозионной защиты, техническая документация на установку для получения водных битумно-латексных эмульсий, смонтирована установка и выпущена опытная партия быстротвердеющей эмульсии. Проведена опытно-промышленная проверка технологии нанесения покрытий на трубы нефтегазовой промышленности.

Ключевые слова: битумно-латексная водная эмульсия, эмульгатор, инициатор, ингибитор, противокоррозионное покрытие, адгезия.

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