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Enhancement of Interfacial Adhesion in Bitumen Coatings by Film-Forming Agents

Alim Feizrahmanovich Kemalov and Ruslan Alimovich Kemalov
Kazan (Volga Region) Federal University, Kazan, Russia

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Abstract: A way for enhancing the interfacial (maltene - asphaltene) adhesion in bitumen coatings is to modify the surface of the disperse phase. For selecting a modifying agent, it should be taken into account that such an agent should have high affinity to both the surface of disperse phase and film-forming agent. Also, high strength and hardness of the coating are required and thermodynamic compatibility, i.e. the solubility parameters for bitumen components should not differ significantly (14.3 - 28.6 $(MJ/m^3)^{0,5}$). The thermopolymer-based film forming agents (TFF) are copolymers of unsaturated hydrocarbons (HC). They are synthesized from by-products formed upon gasoline pyrolysis aimed at preparing ethylene, propylene and other monomers. TFF are successfully used as effective structuring additives to low-viscosity bitumens and petroleum residues. The possibility and practicability of using TFF for this purpose have been proven by investigations performed for a dark TFF, pyroplast. TFF forms a film due to physical (van der Waals or electrostatic) forces rather than as a result of chemical reactions. Comparison of the solubility parameters implies that TFF may prove compatible with aromatic maltenes.

Key words: Thermopolymer-based film-forming agents · Intramolecular structuring · Microscopy · Adhesion-strength properties

INTRODUCTION

Considering the key routes of physico-chemical modification of bitumen coatings [1-11], first it is necessary to select appropriate polymers able to perform intramolecular structuring of the film-forming system of the bitumen. Analysis of the investigation results led to selection of thermopolymer-based film-forming agents (TFF) for bitumen coatings with a solubility parameter of 18 $(MJ/m^3)^{0,5}$, which is close to that of aromatic maltenes, which form coatings with high hardness and optical characteristics.

Some physico-mechanical properties of the TFF are summarized in Table 1

Table 1: Physico-mechanical properties of TFF

Indicator	Value
Density, kg/m^3	950-1170
Softening point, °C	80-95
Aniline point, °C	35-45
Bromine number, g Br_2/100 g	35-45

Under the influence of various factors (air oxygen, temperature, water, ultraviolet rays, chemicals, etc.), structuring of the film-forming agents (formation of new cross links) may continue in the formed coatings, which may finally deteriorate the elasticity and destroy the coatings.

Comparative analysis of the earlier results demonstrates that single-shot blending is inefficient, whereas step-by-step blending of bitumen with polymeric systems improves the compatibility by facilitating the mutual diffusion of polymeric solutions and bitumen and, finally, improves the physico-mechanical properties of the primer. The polymers added to an excessive amount of the solvent are completely dissolved and are better distributed in the bitumen, ensuring high hardness and strength of the coating.

As solvents, we used by-products of distillation of crude oil of the refinery JSC "Tatneftеprom - Zyuzeevneft" and aromatic o-xylene. Thus, the primer was prepared by step-by-step blending of bitumen with the above-mentioned modifying agent:

- Preparation of the polymer solution consisting of TFF, a polymeric plasticizer and a solvent (80-60 wt %%);
- Blending of the polymer solution with the bitumen BN 90/10, 20-40 wt. %, respectively.

Corresponding Author: Kemalov, Kazan (Volga Region) Federal University, Ul. Kremlevskaya 18, Kazan, 420008 Russia.

The first phase of investigations was determination of the optimal content of TFF in bitumen primers A, B, C and D by varying the TFF content from 0 to 50%. Considering the results obtained earlier on the effective blending of bitumen with the distillates used, their solubility and creating the operating viscosity, the weight content of the solvent in bitumen-polymer primers was the same as in bitumen primers. Thus, 60% of the solvent was used for primer A. The formulation of primer B included straight-run oil distillate (SROD), 80% relative to the bitumen-polymer solution. For primer C, sour oil distillate (SOD) at a content of 70 wt % relative to the bitumen-polymer solution was used. Primer D was prepared with black solar oil (BSO) fractions, 75 wt % relative to the bitumen-polymer solution.

The physico-mechanical properties of bitumen-polymer primers A containing o-xylene as the solvent are summarized in Table 2.

The physico-mechanical properties of the bitumen-polymer primer B containing SROD as the solvent are summarized in Table 3.

The physico-mechanical properties of the bitumen-polymer primer C containing SOD as the solvent are summarized in Table 4.

The physico-mechanical properties of the bitumen-polymer primer D containing BSO as the solvent are summarized in Table 5.

It can be seen that with increasing the content of TFF, the drying time and the weight fraction of volatile components decrease; this is caused by crystallization structuring of the dispersing medium of the primer. In all formulations, as the TFF content increases up to a certain range, water permeability decreases and then increases again. For primer A, this range is 0 to 30% TFF; for primer B, this is 0 to 35% TFF; for primer C, the range is 0 to 30%. In the case of primer D, water permeability varies irregularly as a function of TFF content; it increases from 0 to 20% and then decreases again up to the TFF content of 30%. Thus, the data of Tables 2, 3 and 4 indicate that increase in the TFF content from 0 to 30% induces enhancement of the cohesive forces, while adhesion to the bulk material remains almost invariable; therefore, in order to enhance the adhesion and strength behavior, it is necessary to modify the primer by adhesive additives.

According to Tables 5, 6, 7 and 8, among the prepared and studied primer formulations, the most satisfactory water permeability and adhesion characteristics were found for the following primers with the TFF contents presented below:

- Primer A3 (15% TFF relative to the bitumen);
- Primer B5 (25% TFF relative to the bitumen);
- Primer C4 (20% TFF relative to the bitumen);
- Primer D1 (5% TFF relative to the bitumen).

The third phase of primer preparation was to evaluate the structural changes by microscopic examination and to analyze the degree of bitumen dissolution in various solvents.

The visual examination of the formulations of bitumen-polymer primer B shown in Figure 1 indicates that straight-run oil distillate, which comprises mainly saturated alkane hydrocarbons, does not dissolve asphaltenes present in bitumen and is poorly compatible with TFF; as a result, aggregative combinations of bitumen grow in the bitumen-polymer system; finally, this affects the protective properties of the coating. Thus, SROD does not have a dissolving capacity but it is able to impart viscosity to the bitumen-polymer system.

When SOD is used as the solvent, the bitumen-polymer primer C has better solubility characteristics than primer B containing straight-run distillate, because SOD mainly consists of naphthene hydrocarbons and, according to Table 4, contains 22.5% aromatic hydrocarbons. In this system, the bitumen-polymer blend is completely dissolved, which is confirmed by images of the polymer solution shown in Fig. 2; however, when the TFF content is greater than 30%, the temperature of primer preparation increases, because the solvent becomes saturated with TFF and, finally, this leads to polymer precipitation from the solution and affects the protective properties of the coating.

For the preparation of primer D, the bitumen-polymer blend was dissolved in the black solar oil (BSO) fraction with the initial boiling point (IBP) of 350°C, which is formed as a by-product of bitumen oxidation in a Zuzeev bitumen plant. The distillate mainly consists of mixed HC. The weight percentage of aromatic carbon in the "average" molecule of the fraction, C_{arom},% is 12.215. The weight percentage of naphthene carbon in the "average" molecule of the fraction, C_{naph},% is 54.358.

The weight percentage of the paraffin carbon in the "average" molecule of the fraction, C_{par}, % is 33.427. The presence of high-molecular-weight hydrocarbons in the black solar oil cannot be ruled out; this is confirmed by distillate setting point being equal to -5°C and finally by high low-temperature viscosity. The investigation data attest to limited solubility of TFF in BSO and to noticeable increase in the blend preparation temperature following

Table 2: Physico-mechanical properties of primer A containing o-xylene

Primer designation	Drying time, min	Weight fraction of volatile components,%	Water permeability, wt %	Adhesion, kgf/cm^2
A	120	56.5	0.030	1
A1	110	56.2	0.006	1
A2	100	55	0.005	1
A3	100	55.3	0.009	2
A4	90	48.5	0.020	2
A5	90	50.5	0.030	2
A6	90	485	0.040	2
A7	90	50.5	0.090	2
A8	70	55.5	0.040	3
A9	70	48.5	0.100	4
A10	70	45.5	0.100	5

Table 3: Physico-mechanical properties of primer B containing fraction with the IBP of 200°C

Primer IBP-200°C	Drying time, min,	Weight fraction of volatile components,%	Water permeability, %	Adhesion, kgf/cm^2
B	1	60	2.6	0
B1	1	60	2.5	0
B2	0.9	55	2.3	0
B3	0.88	59	2.0	0
B4	0.82	50	1.9	0
B5	0.75	40	1.6	1
B6	0.75	39	1.5	1
B7	0.75	35	1.2	1
B8	0.65	35	1.5	1
B9	0.58	25	1.9	1
B10	0.5	25	2.0	1

Table 4: Physico-mechanical properties of primer C containing SOD

Primer designation	Drying time, hours	Weight fraction of volatile components,%	Water permeability, wt %	Adhesion, kgf/cm^2
C	52	49.0	0.03	2
C1	48	47.5	0.05	2
C2	48	46.5	0.05	2
C3	45	42.4	0.25	2
C4	35	41.9	0.03	2
C5	40	40.0	0.09	2
C6	39	40.1	0.01	2
C7	35	39.6	0.02	2
C8	35	38.2	0.1	2
C9	37	39.5	0.30	3
C10	35	39.2	0.49	2

Table 5: Physico-mechanical properties of primer D containing BSO

Primer	Drying time, hours	Weight fraction of volatile components,%	Water permeability, wt %	Adhesion, kgf/cm^2
D	120	30.9	0.13	2
D1	100	30.2	0.13	5
D2	90	25.2	0.67	2
D3	50	20.2	0.50	2
D4	60	16.0	0.14	2
D5	60	18.0	0.12	2
D6	60	10.5	0.28	2
D7	60	11.5	0.20	3
D8	48	15.5	0.09	3
D9	48	20.2	0.10	2
D10	48	12.2	0.4	2

Table 6: Compositions of roof primers based on BPB

Solvent name	Solvent content, wt %	BPB, wt %	Dissolution temperature, °C	Viscosity of VZh-4 at 20°C, s
SROD, a fraction with IBP 200°C Primer E	80	20	70	15
SOD, a 200-330°C fraction Primer L	70	30	70	25
Black solar oil IBP 350°C Primer S	75	25	80	30

Table 7: Physico-mechanical properties of primers E, L,S

Primer	Drying time, hours	Weight fraction of volatile components,%	Water permeability, wt %	Adhesion, kgf/cm²
E	1	60	2.68	1
L	24	49.0	0.14	1
S	24	30.9	0.20	1

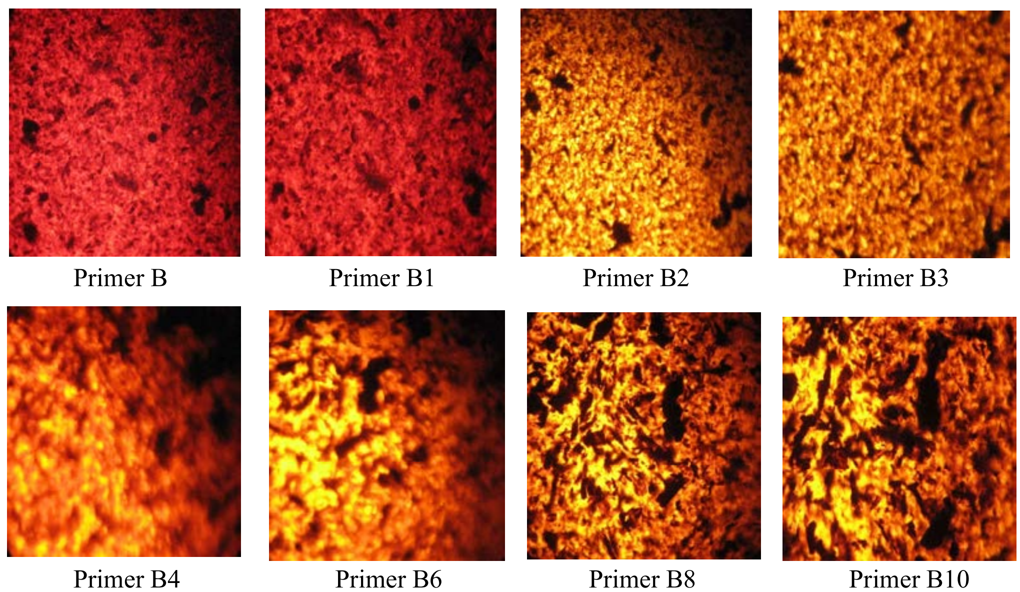

Fig. 1: Visual comparison of the degree of dissolution of bitumen-polymer in SROD

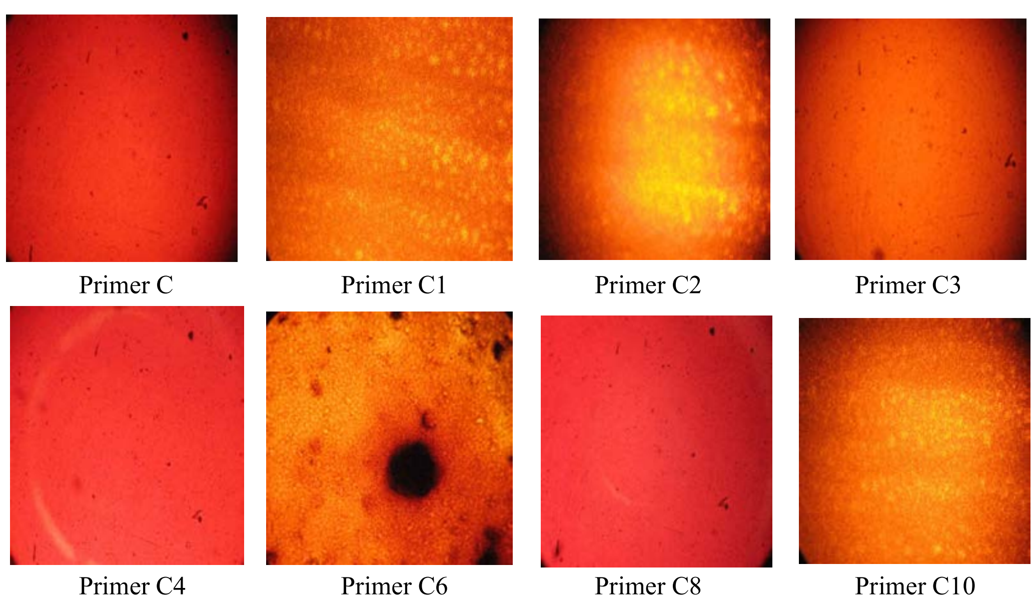

Fig. 2: Visual comparison of the degree of dissolution of bitumen-polymer in SOD

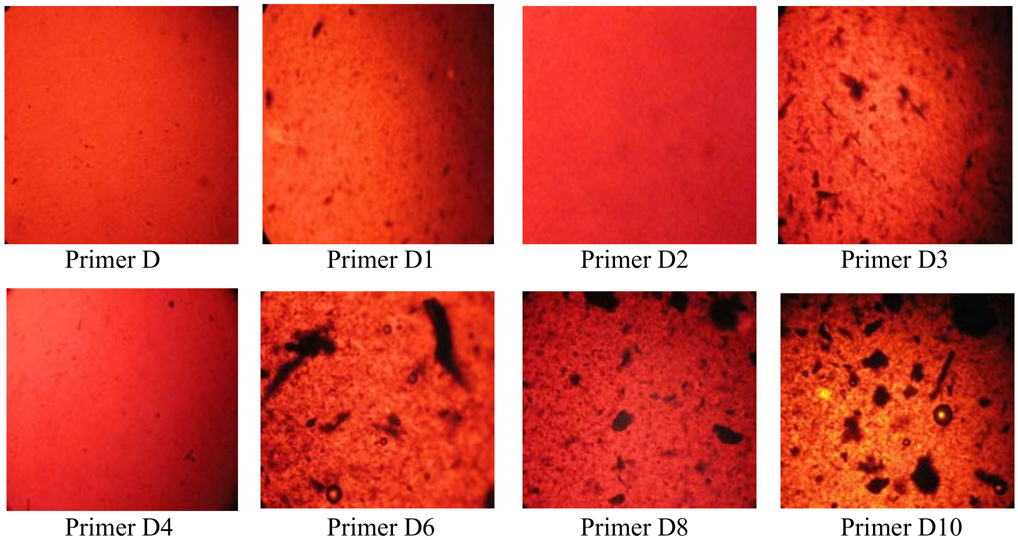

Fig. 3: Visual comparison of the degree of dissolution of bitumen-polymer in BSO

increase in the TFF content above 20%, which can be seen in the images (Fig. 3). The prepared primers were deposited on substrates of concrete foundation (brand 200) and subjected to physico-mechanical investigations. The possibility of film formation on the coating surface is mainly determined, irrespective of the mechanism of this process, by two factors: cohesive forces between the film-forming molecules and adhesive forces between the film-forming agent and the surface being painted. These forces act oppositely. Film-forming agents with strong cohesion were shown to have, most often, weak adhesion and *vice versa*. The cohesive and adhesive forces have the same nature; therefore, they should be considered together.

When the surface being painted has no poorly wetted areas, the attachment of the coating to this surface may be rather strong due to cohesive forces, e.g., a concrete surface painted by a bitumen primer. Bitumen penetrates the concrete pores and is dried inside them; in this case, the strength of attachment to the surface is due to film-forming agent cohesion forces. When the intermolecular bonding is sufficiently strong, the primer penetration depth does not affect the strength of attachment to the concrete.

The fourth phase of the production of primers was selection of the solvent to be used in the roof primer based on the previously developed bitumen-polymeric binder (BPB) [kemalovAFRAdis].

As solvents, we used the following by-products of crude oil distillation at the refinery JSC "Tatnefteprom - Zyuzeevneft:

- Straight-run oil distillate (SROD), a fraction with IBP 200°C;
- Sour oil distillate (SOD), a 200-330°C fraction;
- A fuel oil component (black solar oil), a fraction with IBP 350°C.

The compositions of roof primers are presented in Table 6.

The resulting primers were deposited on concrete (brand 200) and their physico-mechanical properties were studied (namely, drying time, weight fraction of volatile components, adhesion to concrete foundation, water permeability). Physico-mechanical properties of primers E, L, S are summarized in Table 7.

The obtained data for roof primers (Table 7) confirm the previous conclusion that it is more expedient to use SOD as the solvent for the primer; this is indicated by both water permeability of the primer and by visual examination (Fig. 2). Thus, among the obtained test samples of roof primers, the best characteristics were found for primer L.

In the framework of integrated approach to scientific and applied problems aimed to the development of scientific grounds and elaboration of new formulations and production processes for insulating coatings (primers), this communication gives evaluation of the effect of the amount of polymeric additives introduced into a high-melting point bitumen solution in an organic solvent that are able to perform supramolecular structuring of the film-forming system of the bitumen, which has ultimately a beneficial effect on the quality of the resulting primers and enhances the adhesion and strength characteristics of the bitumen film. Additional advantages of the primer as an insulating coating include increase the service life of oil and gas equipment made of reinforced concrete. Upon deposition, the primer diffuses into the concrete foundation. This enhances the adherence between the reinforced concrete foundation and the overlaid insulating material, which considerably increases the service life of the bitumen-polymer insulating roll material.

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