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The study of the gossypol resin impact on adhesive properties of the intermediate layer of the pipeline three-layer rust protection coating

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ABSTRACT

The extrusion technique was used to obtain new compositions of the intermediate layer of the pipeline three-layer rust protection coating. Besides conventional low-density polyethylene and ethylene-vinyl acetate, the composition of the layer included various ratios of exfoliated vermiculite as mineral filler and gossypol resin. The optimal ratios of layer components were determined from the perspective of improvement of adhesion, impact strength, rest resistance, and exfoliation.

The developed compositions fully meet the requirements of current technical standards in this field. Their high technical characteristics are related to the synergistic effect between the gossypol resin and the exfoliated vermiculite. Gossypol resin stabilizes polyethylene and improves the mechanical characteristics of the composition and the mineral filler. Exfoliated vermiculite enhances the interaction of the polymer matrix with the steel.

As compared with the similar compositions, the content of the expensive component – ethylene-vinyl acetate – is reduced from 62–90 wt% to 7–9%.The new composition effectively protects pipelines that operate under high humidity. The developed composition uses cheap local raw materials (including waste, which has a negative impact on the environment) and improves the mechanical properties, rust resistance, and adhesion properties of the obtained coating.

1. Introduction

The need to improve and expand the range of adhesive compositions used in factory and trass rust protection insulation of steel pipelines is dictated by their growing use and the constantly increasing level of technical requirements. The polymeric adhesive underlayer (hot melt adhesive) serves as an intermediate layer in the three-layer coating structure for the rust protection of pipes. Its function is to provide coupling (adhesion) between the outer plastic layer and the inner epoxy layer.

In Kazakhstan, ethylene-vinyl acetate is the only available raw material for such hot melt adhesives. Given the previously obtained positive results [1–5] as regards to the use of mixed ethylene-vinyl acetate compositions as adhesives for metal and liquid epoxy primer, it would be interesting to study the possibility of using them as adhesives in a three-layer coating comprising the inner layer – primer.

When studying the properties of polymer composites, special attention should be paid to the assessment of the contribution of each mixture component to the structure and mechanical properties of composition materials [6]. Using simple mechanical polymer blends, which consist of components with specific properties, is not enough to produce high-quality materials, which can be attributed to the lack of compatibility of most polymers due to the low entropy of their mixture and poor adhesion in the interphase area. The latter fact is one of the main reasons behind phase separation and downgrading of the strength characteristics of the composite materials.

Polyolefin compounds poorly combine not only with the polar polymers, but also with polymers of their own class. The improvement of their technological compatibility requires complex studies on the selection and use of specific compatibility optimizers. Various elastomers are widely used to modify the polyolefin compounds; this improves such properties as impact strength, crack resistance, elasticity and frost resistance [7,8]. The potential for improving the distortion and strengthening parameters of polyolefin mixtures is largely determined by the macromolecular characteristics and monomer composition of initial polymers. However, it is currently impossible to find the optimal values of these factors theoretically. Obviously, the requirements to the macromolecular characteristics and monomer composition of initial polymers providing the improved properties of the compositions cannot be universal; therefore, specifying these structural factors

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with regard to the nature of polymers and their mixture ratios is a relevant problem.

The solidity of the composite material is achieved through adhesion. Such a feature of polymers as adhesion capability allows using them as film-forming materials, for instance, pressurizers, coatings or glues. This parameter also determines the possibility to obtain reinforced and filled polymeric materials. In order to create the adhesive joint, one of the materials should be supple, i.e. fluid (the one that will be adhesive) and the other – quite the opposite - solid (the one that would be the substrate). Adhesion of the substrate coating is the main parameter that determines the quality and reliability of the products [9]. Adhesion also affects the cost of manufactured products, since low adhesion strength is usually found only during the final manufacturing operations.

The main difficulty in choosing the optimal technology that would provide the required adhesion is the lack of objective quantitative criteria for evaluating certain parameters of application, for instance, the purity of the substrate surface and the degree of its activation. In practice, one is often forced to deal with complex systems of several films coming into adhesive contact. In this research, it is a three-layer pipe coating designed for pipelines. The adhesive strength of the system of bodies is determined by their weakest junction. It is worth noting that different junctions may be the weakest ones, depending on the separation conditions.

One of the main factors that determine the adhesiveness of a polymer is its chemical structure. This includes not only the existence and content of functional groups capable of interacting with the surface, but also the spatial structure of the polymer, the presence of side chains and groups, as well as the length and flexibility of the polymer chains or their segments in the netty structures.

Currently, there are a lot of adhesive compositions based on ethylene-vinyl acetate [10–12]. Their disadvantage is the insufficiently high adhesion strength to metals during shift and exfoliation, as well as high concentration of various expensive resins (35–55 wt%).

The purpose of this research is to develop an intermediate layer composition with increased adhesive capacity. Using this layer in the coating composition allows increasing the shifting tension during separation of the adhesive composition of the intermediate layer from the inner primer layer on the one hand and from the developed composite layer forming the outer layer with low surface energy on the other hand.

2. Materials and methods

The suggested new adhesion composition includes four main components: low-density polyethylene (LDPE), ethylene-vinyl acetate (EVA), gossypol resin (GR), and exfoliated vermiculite (EV) as mineral filler.

This research used cheap LDPE with low molecular weight without the stabilizer, since the improving the properties of this polythene is the most relevant task.

Vermiculite is a mineral from the hydromica group; it has a layered structure conducive to many physical and chemical interactions. It is biologically resistant – whereas it is not subject to decay and rot under the influence of microorganisms, it is not a favorable environment for insects and rodents, as well as it is a chemically inert substance – neutral to alkalis and acids.

The new elements in the suggested composition is gossypol resin [13,14]. Gossypol resin is a waste product of cottonseed oil production (tar of fatty acids distillation), a homogeneous viscous mass colored dark brown to black. Gossypol resin contains 52–64% of crude fatty acids and their derivatives. The fat fraction of gossypol resin (FFGS) is dark brown and is a mixture of 11 fatty acids. The specific weight of FFGS is 0.981 t/m^3; its acid number of −112.8 mg KOH/g; saponification value − 228.3 mg KOH/g; ester number – 155.43 mg KOH/g; iodine number – 1.44 g I_2/100 g; solidification temperature − 57 °C. Seven unsaturated acids dominate the compositions (86.8% of total weight), with the largest mass being that of linoleic (30.5%) and oleic acid (26.5%).

Table 1
Content of studied compositions, when compared to the prototype, wt%.

Composition No	LDPE	EVA	EV	GR	FFGS	Talc	APE-silane	Rosin	Mica
1		62–90				1–10	1–5	5–20	1–3
2	78	7		15					
3	78	15	7						
4	78	7	5	10					
5	78	7	5		10				
6	78	7			10	5			
7	73	8	6	13					
8	69	9	7	15					
9	60	11	12	17					
10	85	5	2	8					

The rest are products of gossypol condensation and polymerization generated during oil extraction, especially in the process of distillation of acids from soap stocks. Gossypol resin is used mainly in road construction and as a reagent for removing solid paraffin deposits in oil wells.

The content of the main components in the study of adhesion compositions is presented in Table 1. Hereinafter, all concentrations are expressed in wt%. An adhesion composition based on EVA (composition 1 in Table 1) was used as a prototype for comparison with the developed materials. Such compositions usually contain 62–90% of EVA, 1–10% of talc, 5–20% of rosin, 1–3% of mica, and 1–5% of γ-aminopropiletoksisilan (APE-silane). The other compositions in Table 1, numbered 2–10, offered for study are based on various combinations of LDPE, EVA, GR, and EV. In particular, the concentration of LDPE in the suggested compositions ranges from 69% to 78%, EVA – 7–9%, EV – 5–7%, GR – 10–15%.

A technique for preparing the adhesive layer composition using extrusion was developed. Using extrusion gives important advantages, namely, the possibility to combine several processes in a single extruder: dispersing, mixing, homogenizing, thermal treatment, etc. along with the continuous and highly productive process.

Polymer compositions were prepared by melt mixing in a laboratory desktop multifunction twin-screw extruder UR-TC (England). Its operating principle is fully consistent with the technological process in the production line. The entire rig includes the extruder with dispensers, the cooling bath, and granulator.

Compositions are mixed in an extruder with heating up to 110–120 °C. First, the melted polyethylene and EVA are supplied. Then the exfoliated vermiculite and gossypol resin are added. As the composition moves to the discharge area of the extruder, it its mixed and heated. After a homogeneous mixture is obtained, it is discharged from the extruder at a temperature of 130–140 °C.

The developed compositions' characteristics of adhesion to steel were determined at temperatures of 20 ± 5 °C and 60 ± 3 °C in accordance with standard procedures [15]. Construction low-alloy steel for welded structures ST17G1S (K-52), which is similar to the S355 J0 steel by European classification or 1522 steel by US AISI-SAE classification, was used as the underlayer.

The impact strength was determined by Izod impact testing. The exfoliation area of protective coatings under cathode polarization, the transition electric resistance of the insulating coating was also determined in accordance with standard procedures [16]. The crack resistance of adhesive coatings was studied in a strongly acidic medium at a temperature of 50 °C according to the method described in [17].

The measured properties of tested adhesion layers were compared to the maximum permissible levels according to the standard for protective coatings of steel pipes with a diameter of 820 mm [16]. The rust resistance of the adhesion layer (bloating in groundwater) was measured in the original state after 60-days holding.

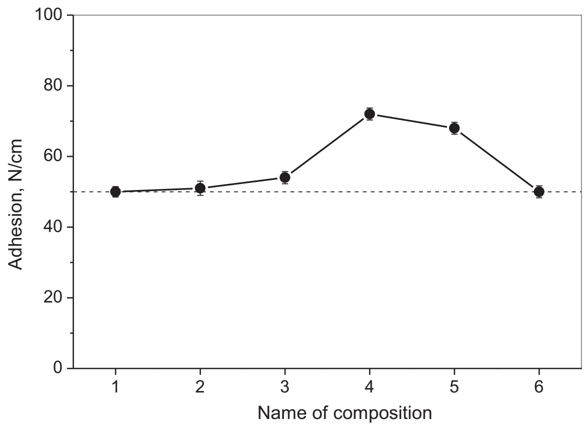

Fig. 1. Impact of the composition content on the magnitude of adhesion to steel at room temperature. The dashed line illustrates the minimum permissible level of adhesion to steel for pipes with a diameter of 820 mm according to standards [16].

The structure of the compositions was monitored using Fourier infrared (IR) spectroscopy in the near and medium wavelength range. Suspension IR spectroscopy was used to study the interaction of polymers with various fillers and modifiers. The crystallinity degree of polymers and phase composition was assessed using X-ray diffraction analysis (Cu-kα radiation). The phase identification was carried out using JCPDS (Joint Committee on Powder Diffraction Standards) data.

With a view to optimizing the content of developed compositions, experiment planning used the LINGO software (Optimization Modeling Software for Linear, Nonlinear, and Integer Programming).

3. Results

The results of adhesion study for compositions 1–6 are presented in Fig. 1. Composition 1 was used for comparison purposes. The other materials are a variation of the content of the suggested four-component adhesion composition (Table 1).

As noted above, the novelty in the suggested composition is the use of gossypol resin. Gossypol resin stabilizes polyethylene and improves the mechanical characteristics of the composition and the mineral filler, which enhances the interaction of the polymer matrix with the steel. The content of the expensive component (EVA) was reduced from 62–90% in prototypes to 7–9% in the suggested compositions (Table 1).

The experiments and mathematical optimization using the LINGO language determined the existence boundaries of the optimal content of composites. The most promising contents are presented in Table 1. The initial adhesion to steel and coating adhesion to steel of these compositions was determined after 1000-h-long water tests at temperatures of 20 °C and 60 °C (Fig. 2). The greatest adhesion was found in composition 4. With minor deviations from the optimal composition, the value change of the measured parameter is 15–30%.

The temperature regime affects the conditions of adhesive contact formation. This factor is especially pivotal when it comes to a melted adhesive. Melted polymer should have certain fluidity in order to fill numerous hollows on the metal surface. The rise of the temperature during the formation of adhesive contact causes viscosity decrease of the melt and ultimately facilitates higher adhesion strength. The results of the study of melt temperature impact on adhesion, measured at room temperature, are presented in Fig. 3. The optimal melt temperature as about 130–140 °C, in which case maximum adhesion is achieved.

In addition to adhesion, the indices whereof are presented in Figs. 1–3, other properties of the developed compositions were studied. Table 2 shows the indices of impact strength, cathodic disbondment, crack resistance, and rust resistance. The properties were measured for compositions 4, 7, 8, 9, and 10 (Table 1) applied to steel pipes with a diameter of 820 mm and tested under high humidity in strongly acidic media.

As noted above, the optimal ratio of components was found in composition 4. Changes in concentration are possible within the set limits, as seen by the example of compositions 7 and 8. However, the melt temperature at the extruder outlet should be 130–140 °C.

All parameters deteriorate if the EVA content is higher than 9 wt% or lower than 7 wt%. Increase in GR content deteriorates the adhesive properties of the composition. Furthermore, the composition does not solidify for a long time. Decrease in GR content to below 10% significantly reduces adhesion and brittleness temperature.

The addition of gossypol resin to the polymer makes achieving contact between the adhesive and the substrate easier and reduces residual strain. However, this also deteriorates the strength properties of the composite. The increase in vermiculite content above 7% reduces the brittleness temperature, while a decrease in its concentration below 5% reduces adhesion to metal and rust resistance.

4. Discussion

Fig. 4 shows data on adhesion to steel (OZ axis) at room temperature of the developed compositions with different content versus the content of exfoliated vermiculite (OX axis) and gossypol resin (OY axis). Various designations were used for experimental points above or below the threshold level of 50 N/cm. This threshold meets the requirements of the standard for oil pipelines [16]. Thus, only the materials of the first group fully meet the requirements of the standard.

The materials of the second group demonstrated insufficient adhesion from the perspective of the new development. The level of adhesion to steel was either 50 N/cm or significantly lower. In spite of the difference in content, all these compositions demonstrated at least one of the three following attributes:

A)total concentration of EV and GR is ≤ 10% (compositions 3, 6, 10),

B) total concentration of EV and GR is ≤ 29% (composition 9),

C) the composition lacks one of the two analyzed components (compositions 2, 3, 6).

Materials with very good adhesion (compositions 4, 5, 7, 8) always had both indicated components, while their total concentration ranged from 15% to 22%. Further research is required to specify the existence interval of compositions with optimal composition in terms of adhesion.

High technical characteristics of the suggested composition are related to the emergence of the synergetic effect between the gossypol resin and the exfoliated vermiculite, since the addition of these components to the composition separately has minimum effect. Other mineral fillers, such as talc or mica, also have little effect (Fig. 1).

The mixing of LDPE and EVA, as well as of various EVAs at certain component ratios and certain difference in the content of vinyl-acetate links in the presence of an “adhesion-active” filler realizes the maximum values on the concentration dependence of adhesive strength connection with metal. The surface of the filler (vermiculite) has increased unsoundness. This determines the presence of the active centers on the surface of the filler, which are capable of forming physical bonds of hydrogen type with the polymer matrix of LDPE + EVA. Thus, vermiculite hardens the composition and improves its heat resistance.

Gossypol resin contains from 52 to 64% crude fatty acids and their derivatives. The rest are products of gossypol condensation, polymerization, and transformation. Gossypol exists in three tautomeric forms. These three forms can be categorized as the aldehyde tautomer, the ketone (quinoid) tautomer, and the lactol (hemiacetal) tautomer [13,18,19]. This implies the formation of at least four intramolecular cycles: the two five-term OH … OH (1.1 ') and two six-term OH…O = C (2,2 ').

Apparently, this chemical structure of gossypol, namely, the presence of four hydroxyl groups at the 6, 6 ' and 7, 7’ position, predetermines its synergistic effect [13]. Aldehyde groups in the gossypol molecule strengthen this effect. It is worth noting that the individual

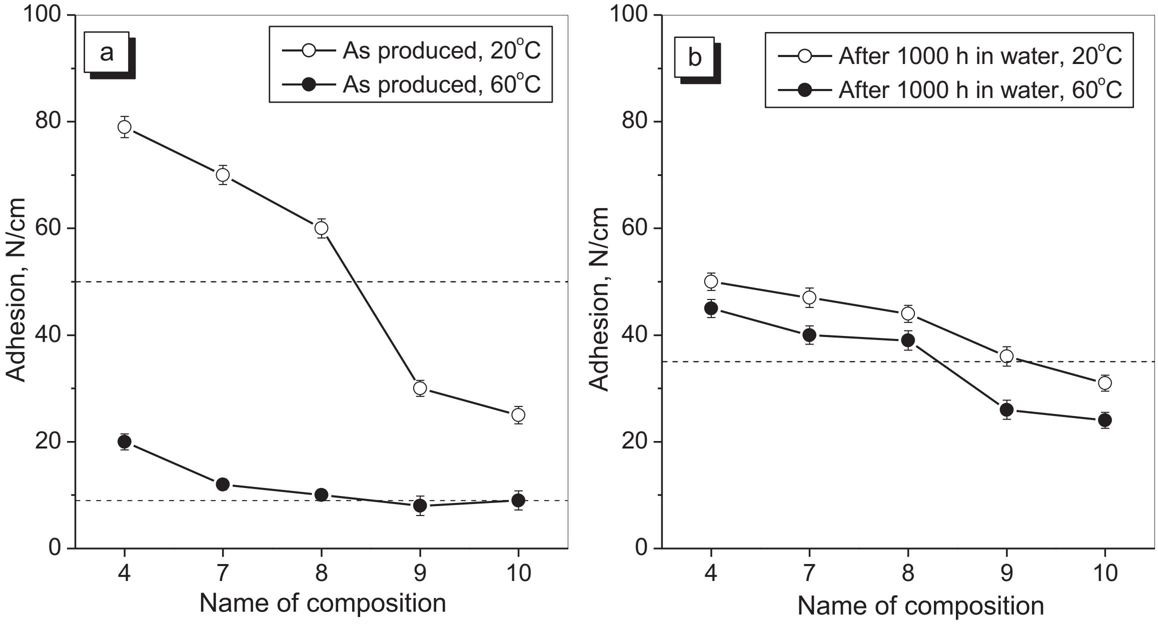

Fig. 2. Adhesion to steel in initial state (a) and after 1000-hour holding in water (b), measured at 20 °C and 60 °C in compositions with different content. The dashed lines illustrate the minimum permissible level of adhesion to steel for pipes with a diameter of 820 mm and appropriate testing conditions according to standards [16].

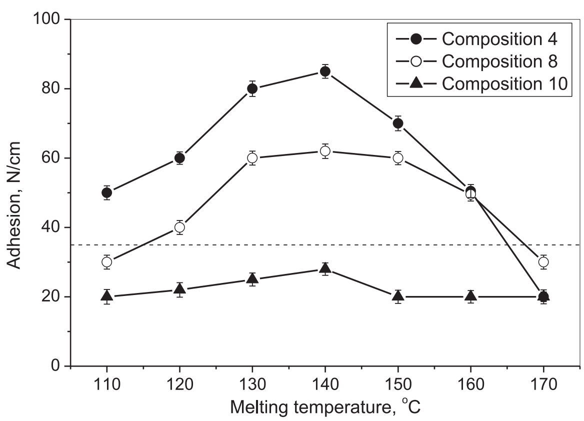

Fig. 3. Dependence of adhesion to steel on melt temperature for compositions 4, 8 and 10. The dashed line illustrates the minimum permissible level of adhesion to steel for pipes with a diameter of 820 mm according to standards [16].

effect of gossypol is much lower than the effect of native gossypol resin.

During the adhesion of the polymer to metal, the role of the adhesive's chemical nature is critical. It is important that the adhesive contains a certain amount of polar groups, while these groups should have the capacity to intensively interact with surface groups of the substrate, for example, serving as electron donors. In addition, various chemical bonds can occur between the metal surface coated with hydrated oxide film and the functional groups of polymers and gossypol.

Full contact in the polymer – metal system may be hindered by permolecular compounds in the melt composition. When the temperature rises, these compounds are destroyed, thus facilitating better adhesive interaction. The rise of temperature not only facilitates the achievement of adhesive contact, but may also result in some

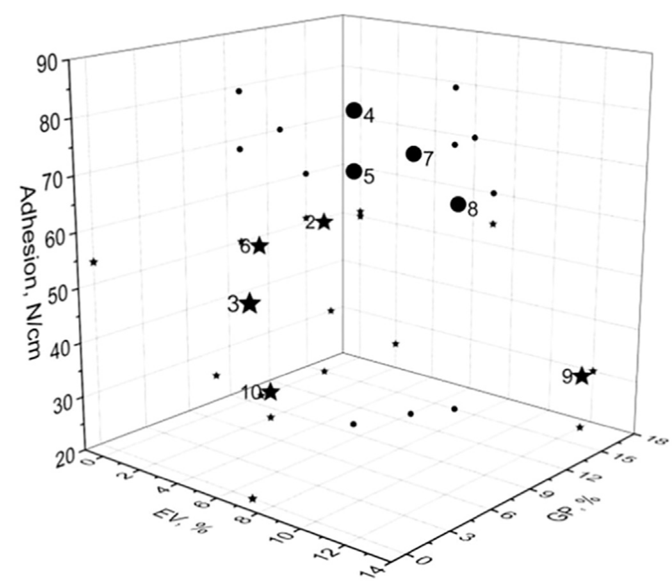

Fig. 4. Adhesion to steel versus the content of EV and GR for compositions 2–10. The compositions with adhesion at room temperature higher than 50 N/cm are marked with circles, below – with stars. The projections of experimental points in a three-dimensional space onto each of the three planes are marked with respective smaller signs.

Table 2
Properties of adhesion compositions 4, 7, 8, 9, and 10, applied to steel pipes with a diameter of 820 mm.

Parameter	T, °C	No.4	No.7	No.8	No.9	No.10	Standard [16]
Impact strength, J/mm of the coating depth	20	5.4	5.8	5.5	4.0	3.1	≥ 5.0
Disbondment area during polarization, cm^2	20	3.0	2.0	2.0	9.0	6.0	≤ 5
	40	3.5	2.5	3.5	12.5	8.5	≤ 10
	60	5.5	4.5	5.5	13.5	13.5	≤ 15
Crack resistance, hours	50	1300	1320	1200	800	600	≥ 1000
Rust resistance (bloating in groundwater) in initial state, %	20	0.14	0.09	0.16	0.21	0.19	n.a.
Rust resistance (bloating in groundwater) after 60 days, %	20	0.10	0.12	0.18	0.22	0.22	n.a.

additional effects, such as to cause the appearance of adhesive functional groups that increase adhesion. The optimal temperature interval is 130–140 °C. In this case, adhesion reaches its maximum and its magnitude is 8.0–8.5 N/cm.

5. Conclusion

A new content of the adhesive layer was developed, which provides for effective protection of pipelines that operate under high humidity. The developed composition uses cheap local raw materials (including waste, which has a negative impact on the environment) and includes LDPE, EVA, gossypol resin, and expanded vermiculite.

The adhesion to steel for the development composition with the optimal content grew by 1.6 times when compared to the prototype – to 80 N/cm at room temperature and to 20 N/cm at 60 °C. In terms of indices of adhesion, impact strength, crack resistance and bloating in groundwater, and exfoliation resistance during cathodic polarization, the developed compositions with an optimal ratio of components fully meet the requirements of existing standards for protective coatings for steel pipes.

High technical characteristics and rust-protective properties of the developed compositions are related to the emergence of the synergetic effect between the gossypol resin and the exfoliated vermiculite. Gossypol resin stabilizes polyethylene and improves the mechanical characteristics of the composition and the mineral filler. Exfoliated vermiculite enhances the interaction of the polymer matrix with the steel.

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