**Results of Research on Obtaining Cation-Type Bitumen Emulsions Based on Gossipol Resin**

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**Abstract:** The article presents the results of preliminary investigations of obtaining oil-free cation-type bitumen emulsions, which are used in road construction on the basis of waste gossipol resin of the oil industry. Initially, the special bitumen compositions for an emulsion based on gossipol resin were obtained, and its physical and mechanical properties were studied. In subsequent studies, the influence of pre-selected emulsifier (sodium oleinate), stabilizer (SaSI2) and acids NSI (SN3SOON, N3RO4) on the extraction properties of a bitumen emulsion was investigated and their optimal ratios were found. The compliance of the resulting content with the requirements of GOST R 58952.1-2020 was studied and recommended for its use in road construction.

**Keywords:** Gossipol resin, anion and cation emulsion, sodium oleinate, colloid mill, mesh sieve,

**INTRODUCTION**

At a time when the requirements for road construction are increasing, the issues of improving the quality of bitumen, its main component, and reducing the pollution are at the forefront. Today, the need for traditional bitumen is increasing day by day, along with the dwindling oil reserves around the world, creating serious problems in the road construction sector. In bitumen production, one of the pressing issues is the creation of a completely new type of bitumen emulsions based on unconventional raw materials: environmentally friendly, durable, economical, cost-effective and simple preparation technologies.

Currently, the use of bitumen emulsions in asphalting roads is one of the promising directions and is considered to be cost-effective, convenient and effective for long-term road maintenance. The purpose of this work is to substantiate scientifically by experimental investigations of cation-type bitumen emulsions from unconventional feedstock- gossipol resin.

Gossipol resin is a waste of the production of cottonseed oil, which contains hydroxyl (−OH), carboxyl (−COOH), carbonyl (−COH) and amine (−NH2) groups, as well as molecules that combine several functional groups, which affect the general properties. These groups have a high activity when thermally oxidized, and their ability to react with inorganic and inorganic matter increases several times. By modifying the Gossipol resin with various stabilizers and platifiers, it becomes possible to produce environmentally friendly and sustainable bitumen products.

Scientists from Uzbekistan and the world are conducting research on the processing of gossipol resin and production of bitumen binders as a substitute for petroleum products, production of anticorrosive products. This will not only serve to reduce environmental problems but also to generate economic benefits, ending the dependence on oil that is running out of production of these types of products.

The influence of temperature and catalyst on dehydration and thermal oxidation of gossipol resin has been investigated by research scientists R. Jabbiev and others. It has been found that it is optimal to carry out the oxidation process in support of Fe2O3 and H3PO4 catalysts at 210-220°C. In thermally oxidized gossipol resin, it has been shown to increase the reactivity capacity of functional groups. The effect of CaO on the Gossipol sediment was found to be that the chemical and physico-mechanical properties of the composition approximate those of petroleum bitumen. The scientists observed that increasing the CaO content from 0.5% to 2.0% as a result of copolymerization of gossipol resin at 220°C increased the softening temperature of product from 51°C to 62°C and decreased penetration from 62 mm to 34 mm [1].

Jumaniyazova D. and others developed anti-corrosion composite materials to protect ferrous metals from corrosion on the basis of gossipol resin. These composite materials have been tested in St3 category steel samples under conditions containing varying concentrations of variable concentrations of H2SO4, HNO3, and HCl at different temperatures. According to the test results, the optimized composition provided 91.0-93.1% protection of St3 steel exposed to 20-40% H2SO4 solutions at a temperature of 50-100°C for 24 h. Similarly, at temperatures of 25-30°C, the protection level reached 88.2-88.9% in 20–40% HNO3 solutions[2].

Jumaniyazov M. et al. investigated the scientific foundations of synthesis of oil-free sealants suitable for the production of materials insulated on the basis of cotton oil production waste, gossipol resin and local resources, as well as the possibilities of their application. It has been found that the newly created compound can withstand high temperatures (up to 97°C) while does not degrade at low temperatures (down to -20°C) [3].

N. Sh. Otarbaev made new demulsifiers on the basis of gossipol resin and their effect on emulsion stability and decay rate was evaluated. The aldehyde and phenolic groups within gossipol react with the surfactants inside the bitumen emulsion, ensuring a faster decomposition of the emulsion. Emulsion drying time was reduced by 25–35% in mixtures where a modifier based on 1–3% gossipol resin was used. These results resulted in enhanced adhesion between coating layers and a faster reinforcement of the compound [4].

B. Rakhimov, B. Adizov and other researchers evaluated the adhesion properties of bitumen to mineral surfaces and found in the results a significant effect of gossipol resin on the adhesion strength. When Gossipol resin was added to the emulsion at an amount of 2%, the contact angle decreased from 82° to 46°. This showed increased wetting and adhesion to the surface. The surface strength of bitumen was found by 28% on surfaces treated with modified binder. This is an important result, especially for adhesion under humid conditions [5].

The influence of organic binding additives on bitumen quality was studied by scientists S. G. Kakabaev and R. Nurbersiev. Gossipol resin based modifications have shown to increase viscosity, frost resistance and resistance to deformation when immortalized to an emulsion at ratios of 3% and 5%. Notably, the bonding strength is increased by 1.2 times. These results improve the performance of bitumen emulsions under low temperature-temperature conditions [6].

In the research of M. Yu. Ismailov and other researchers the physicochemical properties of bitumen binders prepared by gossipol resin were investigated. According to the study, the oxidation resistance and thermal stability of bitumen binders prepared using gossipol resin were tested. According to the test results, the bond density and viscosity increased by up to 20% when 2.5–4% of gossipol resin was added. There was also increased hydrophobic activity and increased water resistance within the structure. This approach has been shown to provide an environmentally friendly and efficient binder based on inexpensive raw materials [7].

Research scientists **Otarbaev, N.S.** The viscosity, heat stability and liquid resistance of bitumen binders modified with gossipol resin were analyzed by others. Modified bitumen binders enriched with 4% gossipol resin showed a 30–35% improvement in elasticity and adhesion indices. The mechanical stability of the mixture has also increased, and it has been found suitable for long-term application [8].

It has been investigated by xu, L. and other scientists that by adding water-based acrylate polymer to an asphalt bitumen emulsion, can improve the coating stability and adhesiveness. As the ratio of acrylate to bitumen emulsion increased, the dispersion stability increased, which in turn resulted in improved surface protection properties [9].

According to the research of the presenting scientists Babagoli, R., Ameli, A., Shahriari, H., styrene-butadiene-styrene modified bitumen emulsion mixtures have a higher mechanical stability than conventional bitumen emulsions. This has been found to give the polymer bitumen elasticity, enhance viscosity, and provide resistance to deformation [10].

The process of preparation of bitumen samples modified by polyethylene waste and their stability indicators were evaluated experimentally by Fang, C. and other scientists. By increasing the content of polyethylene, the mechanical properties of bitumen are improved, especially its resistance to heat and deformation increases. The processing process, i.e. the preparation temperature and the mixing speed, have significant influence on the stability level. The highest stability was observed in the sample, which was treated at 180°C temperature for 30 min. This has been shown to enable efficient use of waste [11].

The influence of process parameters, namely emulsifier quantity, mixing rate and dispersion time on the physicochemical properties of emulsion of emulsion have been investigated by Gingras, J. et al. researchers in the preparation of bitumen emulsions. Particle diameter, viscosity and stability of an emulsion were cited as key indicators in the study. The optimal size of the emulsifier as the viscosity-increasing factor has been determined. The study contributes to the formulation of control parameters in order for emulsions to experiment in industrial settings [12-14].

The peculiarity of the results of scientific research, referred to in this article, is that for the first time in the world practice bitumen emulsions of cation type are proposed in the world practice.

**METHODS**

We used the VUB-1 apparatus to determine the conditioned viscosity of the emulsion. Tests were performed on two parallel samples at the same time. And it was done. The emulsion delivered to a temperature of (20 ± 0.5) °C was poured into the working cylinder of the apparatus in the closed loop state to the mark marked on its surface and thoroughly mixed with the help of a thermometer, its accurate temperature was recorded. After that, the thermometer was taken out and the apparatus was immediately opened. When the emulsion level reached the 25ml mark per retaining cylinder, a stopwatch was triggered. When reaching 75 ml, the stopwatch was stopped and the duration of the discharge was determined in seconds. A flow time of 50 ml of an emulsion (in seconds) was taken as an indicator of its conditioned viscosity. The tests were performed on two parallel samples and the final result was obtained at the arithmetic mean of the two tests.

To determine the residue in the sieve, a mesh sieve No. 014 was used. The sieve, previously washed and dried with gasoline, was pulled out along with the bowl, and then the sieve was moistened with a 1% hydrochloric acid solution. For analysis, an emulsion of 100 g was prepared, and its nozzle was passed through a sieve evenly; In this process, using a glass straw, the upper edge of the sieve was lightly shaken and knocked. Water with a residual acid solution remaining in the sieve was thoroughly transparent and washed until the emulsion traces disappeared. When washing was finished, the sieve was placed in a porcelain cup and dried to a continuous mass at a temperature of (105±5)°C. Afterwards, it was cooled to room temperature and pulled together with the cup The remaining parameters of the emulsion were determined in compliance with the requirements given in GOST R 52128-2003. M = (g3 - g1) / (g2 - g1) ·100. Here: g1 is the mass of the codic mass measured together with a cup and a stick, g; g2 – mass of the emulsion, measured with a cup and a stick, g; g3 – residual mass of the water-evaporated emulsion, measured with a cup and a stick, g.

## Physico-mechanical properties of the emulsion were established after the evaporation of the water contained in it. Depth of needle dip [GOST 11501](https://meganorm.ru/Data2/1/4294852/4294852830.htm) Softening temperature, according to requirements [GOST 11506](https://meganorm.ru/Data2/1/4294852/4294852826.htm) Elongation and elasticity according to the requirements of [GOST 11505](https://meganorm.ru/Data2/1/4294852/4294852827.htm) requirements.

**RESULTS AND DISCUSSION**

At the beginning of the research, we investigated for obtaining the ingredients suitable for the preparation of bitumen emulsions based on gossipol resin. For this purpose, oilless bitumen was synthesized into thermooxidized gossipoli resin under special conditions by introducing polymer matrix-forming components (CaO), plasticizers (rubber resin, sulfur) and stabilizers (polyethylene, soapstoke). Physical-mechanical properties of the obtained oil-free bitumen are presented in Table 1.

**TABLE 1.** Physico-mechanical parameters of oil-free bitumen used in the extraction of bitumen emulsions

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| No | Oil-free bitumen brand | Needle penetration depth, not less than 0.1mm, | | The softening temperature of ring and ball is not lower than °C, | Stretchability, cm, not less than | | Flash point, °C |
| 25 °C | 0 °C | 25 °C | 0° C |
| 1 | BG 60/90 | 71 | 23 | 47 | 62 | 3,8 | 250 |
| 2 | BG 90/130 | 98 | 19 | 44 | 80 | 5.7 | 250 |

The table data can be seen that the non-neutered bitumen obtained for the study comply with the standard requirements of bitumen indicators used to obtain emulsions.

Further research focused on the preparation of a bituminous emulsion based on the selected oil-free bitumen. Inside the research was carried out on special equipment equipped with stirrer and heating. Pre-measured bitumen was laid into the equipment and heated to a temperature of 140 °C.

In the next stage of the research, we focused on the synthesis of oleylamine hydrochloride, an emulsifier used in our studies on obtaining cationic bitumen emulsions, in laboratory conditions.

The synthesis process was carried out as follows. First, we reacted oleic acid with ammonia. As a result, we obtained amides through the following reaction.

C₁₇H₃₃COOH + NH₃ → C₁₇H₃₃–CONH₂ + H₂O

Then, we hydrogenated the resulting amide with hydrogen H2 to obtain amines.

C₁₇H₃₃–CONH₂ + 2H₂ → C₁₇H₃₃–CH₂–NH₂ + H₂O

Later, we reacted it with a hydrochloric acid solution to obtain oleylamine hydrochloride. This reaction occurs as follows:

C₁₈H₃₇NH₂ + HCl → C₁₈H₃₇NH₃⁺ Cl⁻

The reaction conditions are as follows: In laboratory conditions, 1 mol of liquid oleylamine was taken and mixed with 15 ml of dichloroethane in a flask. The solution in the flask was cooled to -3-5 °C. Then, 36% HCl solution was gradually added to the solution with constant stirring. Crystals of oleylamine were observed to precipitate in the flask. After the formation of the precipitate stabilized, the mass in the flask was left on ice at a temperature of -3-5 for 30 minutes. Then, the precipitate was filtered off and purified from unreacted substances in a cold ether solution and dried at 35-40 °C. In this sequence, oleylamine gyrochloride was synthesized and prepared for use as an emulsifier.

It is well known that in the preparation of stable bitumen emulsions, the amount of components involved in the process, the selected conditions, the mixing intensity and particle size in the content play an important role. For this purpose, 5 samples consisting of different volumes of bitumen, emulsifier, stabiliser and acid were prepared and different temperatures and pH were selected during the process, in order to find the optimal parameters to obtain stable bitumen emulsions. Prepared samples and conditions are presented in Table 2 below.

**TABLE 2.** Bitumen used in the process of extracting emulsions components and process conditions

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| № | BG 90/130 Bitumen, % | Bitumen temperature, °C | Emulsifier and stabilizer solution, % | | | | Solution temperature, oC | Solution, pH | Colloid mill intensivity,  rpm | Bitumen emulsion formation time, minutes |
| C18H37NH2·HCl | CaCl2 | HCI | H2O |
| q | 60,0 | 140 | 0,15 | 0,1 | 0,1 | 39,65 | 40 | 2,0 | 3000 | 30 |
| 2 | 60,5 | 142,5 | 0,16 | 0,125 | 0,125 | 39,09 | 41 | 1,9 | 3000 | 35 |
| 3 | 61,0 | 145,0 | 0,17 | 0,150 | 0,150 | 38,53 | 42 | 1,8 | 3000 | 40 |
| 4 | 61,5 | 147,5 | 0,18 | 0,175 | 0,175 | 37,97 | 43 | 1,7 | 3000 | 45 |
| 5 | 62,0 | 150,0 | 0,19 | 0,2 | 0,2 | 37,41 | 44 | 1,6 | 3000 | 50 |

As can be seen from Table 2, our own synthesized oil-free bitumen composite BG 90/130 was used. Its characteristics are close to that of petroleum bitumen BND 90/130 branded bitumen. The tests were carried out at temperatures (140- 150°C) at various temperatures of bitumen. Hydrochloride oleylamina (C₁₈H₃₇NH₂· HCl), 0.15–0.19, CaCl2 content 0.1–0.2, HCl 0.1–0.2 and water content 39.65–37.41%. The serial studies determined different solution temperatures 40-44 °C, rN 2.0-1, colloidal milling intensity 3000 rpm.

The method for preparing an emulsion based on gossypol resin-based petroleum-free bitumen was carried out in the following steps. The previously prepared petroleum-free bitumen was heated in a special container equipped with a stirrer and at a temperature of 140 ° C. Then, in a second container equipped with a stirrer, oleylamine gyrochloride emulsifiers were prepared in 5 samples according to the recipe given in the table above. Calcium chloride (stabilizer) was added to it in the above amounts to 5 samples and mixed thoroughly. After that, hydrogen chloride (HCl) was added to each sample and the pH values ​​of the solution were obtained as given in the table. The prepared solution with emulsifier and stabilizer was heated to 40 ° C. After that, the colloid mill was heated to a temperature of 90 ° C. Then, an aqueous solution of the emulsifier was first added to it and milled for 10 minutes. Bitumen was then added to the mill. The temperature in the mill was maintained at 90 °C and it was operated for 30 minutes. As a result, emulsions with a particle size of 5-7 μm were obtained. Quality indicators of obtained emulsions were comparatively analyzed.

**TABLE 3.** Investigation of the residual mass determination of oil-free bitumen emulsions in mesh sieve №14

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| № | Bitumen  mass,% | Mass of the emulsifier solution,% | Residual mass of cation bitumen emulsion in mesh sieve No 014,% | Solution pH |
| 1 | 60,0 | 40,0 | 0,33 |  |
| 2 | 60,5 | 45,0 | 0,30 |  |
| 3 | 61,0 | 50,0 | 0,28 |  |
| 4 | 61,5 | 38,5 | 0,25 |  |
| 5 | 62,0 | 60,0 | 0,24 |  |

As can be seen from the results of Table 3, the residual mass of non-oiled bitumen prepared by gossipol resin and 55% of emulsifier solution of our 4th structure in mesh sieve №014 was 0.48% for anion bitumen emulsions, 0.25% for cation bitumen emulsions, and the stability of the compositions was established.

The results of the comparison of the main physical mechanical properties of the created oil-free anion and cation type bitumen emulsions with their analogous compositions are presented in Table 4**.**

**TABLE 4.** The main physical and mechanical properties of created emulsions

|  |  |
| --- | --- |
| **Pointer Names** | **Norms of pointers** |
| Appearance | A Kind of Resin Emulsion Mass |
| Color | From dark brown to black |
| Smell | Specific |
| Binder and emulsifier quantities | 62,03 |
| conditional viscosity of 20°C, s | 56 |
| No. 014 is not much of a residue in a mesh sieve, but %  7 day after  30 days later | 0,25  0,6 |
| The needle dipping depth of the binder at 25°C is not less than 0.1mm, | 61 |
| The needle dipping depth of the binder at 0°C is not less than 0.1mm, | 20 |
| The bonding softening temperature, not lower than °C | 48 |
| Stretch capacity of binder at 25°C sm, not less than | 54 |
| The stretch ability of the binder at 0°C is sm, not less than | 3,4 |
| Burning point, °C, | 250 |

The data presented in the table show the physico-mechanical properties of bitumen obtained on the axis of non-oil-free bitumen It complies with the guidelines given in GOST R 52128-2003.

**CONCLUSION**

As a result of scientific research, it was possible to obtain new types of oil-free bitumen emulsions, which are used in road construction on the basis of gossipol resin. Under laboratory conditions, emulsifier can induce a hydrochloride to release oleylamine (C₁₈H₃₇NH₂· HCl) based on oleic acid (C₁₈H34)O2 optimal parameters have been created.

The main binder of the emulsion used in the research is the gossipol resin based extraction of bitumens from bitumen. For this purpose, the waste of oil-and-oil production - gossipol resin - is thermally oxidized, and corresponding polymer-forming agents (CaO, urotropin), plasticizers (rubber powder, sulfur), stabilizers (H3PO4), fillers (polyethylene and rubber waste) are introduced into it

Non-oiled bitumen of the 90/130 brand was obtained.

The optimal conditions for obtaining stable oil-free bitumen emulsions and optimal emulsifier ratios were found. At this point, the aggregate homogeneity of bitumen emulsion at 140 °C and the optimum temperature of emulsifier solution of 60 °C is determined and furthermore the bitumen emulsion formation temperature does not exceed 90 °C.

Based on the results obtained, the mass fractions of the bitumen and emulsifier solution were determined in order to form cation-type bitumen emulsions. In this case, the optimal composition of oil-free bitumen emulsions by means of a mesh sieve No014 optimal composition was selected according to GOST R 52128–2003. According to the results of the study, with a non-oil-free bitumen mass of 45% and the mass of emulsifier solution 55%, according to GOST P 52128-2003, the residual mass of anion-type bitumen emulsion №014 in a mesh sieve is 0.48% and the residual mass of cation-type bitumen emulsion №014 in a mesh sieve is 0.25%.fully meets the requirement of GOST P 52128–2003.

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