UDC 665.775.625.85

PREPARATION OF BITUMINOUS MATERIALS BASED ON NEUTRALIZED ACID TAR

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The article presents the results of the study on neutralizing acid sludge from the production of sulphonate additives by the JLLC "LLK-Naftan" with dolomite flour and chemical water slurry obtained with the help of bituminous roofing hot mastics corresponding to the requirements of GOST 2889 on the basis of neutralized products. The proposed technology makes it possible to expand the raw material base resources for obtaining bituminous materials through the use of product waste and to reduce the cost for obtaining bitumen mastics.

Introduction. Acid tar is formed by sulfuric acid purification of mineral oils, by the production of sulfonate additives, in alkylation processes where sulfuric acid as a catalyst is used. This type of waste causes a serious environmental problem. Acid tar accumulates in dumps and open storage ponds where the acid is washed out by atmospheric precipitation and as a result SO2 and SO3 is released. This results in of water and air contamination. Acid tar is one of the most difficult products to waste dispose.

At the same time the acid sludge is a valuable secondary material resource for certain products including commercial petroleum products. The constant need for the commercial petroleum products such as road bitumen, roofing mastics and others with a relatively high cost necessitates the search for new ways of their obtaining, including the usage of less expensive components of raw materials, in particular, acid tar.

The analysis of certain studies has shown that there are various methods for processing acid sludge while producing bituminous materials. They involve the process of their neutralization with the help of an aqueous solution of alkalis, the process is accompanied by the formation of a large amount of sewage, what is more, alkalis is an expensive reagent [1]

The purpose of this study is to observe the process of the neutralization of the acid tar during the production of the sulfonate additives at JLLC "LLK-Naftan" with dolomite flour and chemical water treatment sludge at the CHP plant, produced on the basis of the neutralization products of bituminous materials.

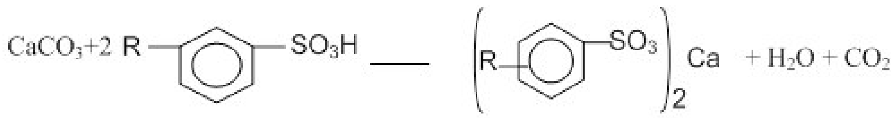
Methodology. As a neutralizing agent one can use a natural mineral – dolomite flour, produced according to GOST 14050-93 of JSC "Dolomite", Vitebsk city (pH = 7.45). As a second neutralizing agent one can use a chemical water treatment slurry from Polotsk CPP (pH = 10.51) which has not found its qualified application until recently and is accumulated in dumps.

The treatment of acidic tar is carried out in two stages. At first stage, the acidic tar is heated to a temperature of 80-110 C and is mixed with neutralizing agents, dolomite flour and slurry are added at 5, 10, 15 and 20 wt. on tar. The neutralization time is 20 minutes.

The main reactions of neutralization of sour tar are the following:

$CaCO_3 + H_2SO_4 = CaSO_4 + H_2O + CO_2$

$MgCO_3 + H_2SO_4 = MgSO_4 + H_2O + CO_2$



The acid number is determined as follows: the sample of acidic tar is dissolved in the benzene-kerosene mixture, the distilled water is added and mixed, so that the soluble organic sulfonic acids are transferred into water. The resulting system is poured into a separating funnel and is left to rest for 24 hours before the emulsion is separated into two layers. The aqueous part is titrated with 0.1 N sodium hydroxide solution.

To determine the total acidity a method of direct titration is used, this method was proposed by B.M. Rybak and I.E. Blumin. The method consists of the following: the tar weight is dissolved in neutralized alcohol-benzene solution and is titrated with 0.5 N aqueous NaOH solution in the presence of phenolphthalein indicator. Total acidity is determined with the formula:

$$K = \frac{T_{а,в} \cdot 24.5 \cdot 100}{A \cdot C \cdot 20 \cdot 100}$$

where *K* is the total acidity, %;

$T_{a,в}$ – titre 0.5 N solution of alkali, titre is 0.5 n solution of alkali, 24.5 is the weight 0.5 g-eq H_2SO_4;

A is a hinge of tar, g; C is the amount of extract taken for the titration, ml; 20 is the weight 0.5 g-eq. NaOH.

Results, discussion and conclusion. The characteristics of the initial sample are the following: acid sludge produced by the sulfonate additives of JLLC "LLC-Naftan" are presented in the table. Acid number, acidity, ring softening temperature as well as the ball and needle penetration depth at 25 ° C and the content of individual components are also determined. The starting sample is a black solid sticky mass with a sharp specific odor, by its consistency resembles clay.

Under the action of static loads it exhibits named properties of non-Newtonian liquids.

Table 1. – The main characteristics of acid sludge taken from the Sulphonate Additives Plant at JLLC "LLK-Naftan"

Rate	Implication
Acid number, mg NaOH/g	117,073
Inorganic acidity, %	11,339
Softening point on the ring and ball, °C by GOST 11506	45,5
The depth of needle penetration at 25 °C by GOST 11501	138,4
Rate of components, % mass.	
Sulphonic acids in terms of group $–SO_3H$	up to 25
Dipping acid	up to4
Oil (I,II,III groups of aromatic and naphthenic-paraffinic hydrocarbons)	up to 60
Asphaltene	up to 10
Pitch	up to 15

The acid tar is neutralized with dolomite flour at various temperatures. It is established that the degree of change in the acid number is approximately the same at 80, 90 and 100 ° C and significant decrease in the acid number by more than in 2 times is relative to the initial value which is found upon neutralization at 110 C. This is probably due to the fact that during heat treatment of acidic tar at 110 ° C there is low-temperature decomposition. It consists in the interaction of sulfuric acid with resinous-oil and resinous-asphaltene substances of the organic part of acidic tar which acts as organic reducing agents. This process also helps to reduce acid number. Similar dependence is also established for the acidity index. Maximum reduction is established when it neutralizes with dolomite flour and heat treatment of acid tar at 110 ° C. With this temperature the residual acidity after neutralization is only 0.61% which indicates the absence of water-soluble acids.

Analysis of the change in the softening temperature of acid sludge after neutralization with dolomite flour at various temperatures has shown that the increase in the heat resistance and temperature of softening of tar is observed throughout the temperature range of processing. The highest values are recorded at a temperature of 110 ° C. The rate of increase in the change in the softening temperature increases with increasing processing temperature. Thus, with a 5% addition of flour for neutralization at temperatures up to 100 ° C the softening point increases by no more than 1.5 ° C, and at 110 ° C the softening temperature increases by 6 ° C. Probably, this is due not only to the influence of dolomite flour, but also to the chemical reactions of low-temperature decomposition. Thus, the percentage of addition of the neutralizing agent and the neutralization temperature has a significant effect on the target parameters.

Figure 1 shows the dependence of the change in the acid number of sour tar after neutralization with dolomite flour and chemical water treatment sludge at a temperature of 110 ° C. It can be seen that the neutralization process is more effective when one uses chemical water treatment sludge which correlates with the pH of the neutralizing agents.

The same dependence can also be traced from a change in the acidity of tar after neutralization with dolomite flour and chemical water treatment sludge. At the same time any almost neutral product can be obtained with the addition of a chemical water treatment slurry of about 10% by weight as well as the same acidity value only with a 20% additive of dolomite flour. Thus, chemical water treatment sludge is needed twice as much to neutralize acid sludge than dolomite flour needs.

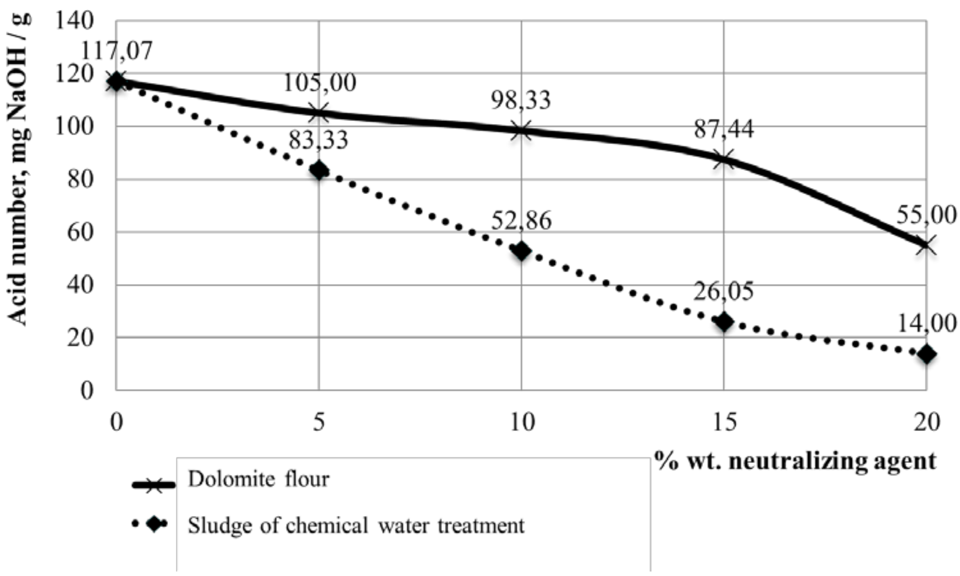


Fig. 1. The dependence of the acid number
of acid sludge upon neutralization with dolomite flour and chemical water treatment sludge
at a temperature of 110 ° C

The linear dependence of the change in the softening temperature according to the softening temperatures on a ring and a sphere acid sludge after neutralization with dolomite flour and chemical water purification slurry at a temperature of 110 ° C is determined (reliability of the approximation R2 = 0.9 for dolomite flour and 0.94 for the slurry). It was found out that at concentrations of the neutralizing agent up to 10% by weight the softening point increases by almost 6-8 ° C, and at a higher concentration of more than 15% by weight heat stability is increased to a greater extent from slurry chemical water purification.

Based on the products of neutralization of acid tar it is proposed to obtain bituminous roofing bitumen according to GOST 2889 since various dust-like fillers and, in particular, fine-grained dolomites are used to produce this mastic.

As a bituminous binder for the preparation of mastics two samples are used: oil road bitumen 60/90 and bitumen of oil 90/10. For initial samples their softening temperatures are determined according to the softening temperatures on a ring and a sphere (for oil road bitumen 60/90: 53 ° C, for bitumen of oil 90/10: 110 ° C) and the penetration depth of the needle at 25 ° C (for oil road bitumen 60/90: 68.4 x 0,1 mm, for bitumen of oil 90/10: 15 × 0.1 mm).

As a component of the mastic, bitumen binder is added in concentrations of 10, 15 and 20% by weight. The product is neutralized by slurry chemical water treatment at a temperature of 110 ° C.

The analysis of the dependence of the penetration depth of the needle at 25 ° C for bituminous mastic after addition of the neutralizing acid sludge shows that the obtained additive has practically no effect on the penetration rate of bitumen of oil 90/10 with initially high content of asphaltenes but the addition of a neutral product to the road bitumen oil road bitumen 60/90 leads to a significant increase in its hardness for more than twice the penetration depth of the needle when 20% of the neutral product is involved. The reason is probably the increase in the content of asphaltenes.

The analysis of the dependence of the change in softening temperature of bitumen mastic after addition of the product of neutralization of acid sludge shows that the mastic softening temperature on the basis of oil road bitumen 60/90 is increased, since the neutral product with a softening point of 60 ° C is added and, probably, additional processes structuring and the heat resistance of the mastic based on bitumen of oil 90/10 deteriorates because a more fusible component is added to it.

For bituminous mastics, the temperature of brittleness in the freezer compartment is determined, flexibility and heat resistance according to GOST 2889, the results obtained are shown in Table 2, it is established that the obtained values do not exceed the normative values for Mastic bituminous roofing G-65 and Mastic bituminous roofing G-85.

Table 2. – The characteristics of bitumen mastics based on neutral acid sludge

Indicator name	Mastic bituminous roofing G-65 by GOST 2889	oil road bitumen 60/90 and 15% of the mass of neutral acid tar slurry (15% by weight, 110 ° C)	Mastic bituminous roofing G-85 by GOST 2889	bitumen of oil 90/10 and 15% of the mass of neutral acid tar slurry (15% by weight, 110 ° C)
1. Heat resistance for 5 hours, C°, not less than	65	65	85	85
2. Softening temperature by the "ring and ball" method, ° C°	68–72	74,5	88–92	102
3. Flexibility at temperature (18 ± 2) C° on a rod in diameter, mm	15	15 (resist)	30	30 (resist)
4. Filler content,% by weight: pulverized	25-30	up to 15	25-30	up to 15
5. Water content, % mass.	Trace	no	Trace	no
6. Temperature of embrittlement of bituminous binder, C° not higher	–15	lower –15	–12	lower –12

Thus, it can be concluded that the product of neutralization of acid sludge from the production of sulfonate additives by JLLC "LLK-Nathan" by chemical water treatment slurry from Polotsk CCP plant can be disposed of by mixing with bituminous binders and obtaining bitumen roofing hot mastics that meet the requirements of GOST 2889. For neutralization dolomite flour is used but with double volume for neutralization.

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