European Journal of Mechanical Engineering Research
Vol.3, No.2, pp.42-49, May 2016
Published by European Centre for Research Training and Development UK (www.eajournals.org)

SECONDARY PRODUCTS OF PETROCHEMISTRY IN PRODUCTION OF BITUMEN EMULSIONS

Valikhan K. Bishimbayev[1], Kuandyk V. Bishimbayev[1], Tynlybek S. Bazhirov[1], Eugene F. Glady[2], Alim F. Kemalov[2], Ruslan A. Kemalov[2]

[1]M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan
[4]Kazan Federal University, Kazan, Russian Federation

ABSTRACT: *Today, the most important tasks of petroleum processing and petrochemistry are provision of a deep processing of heavy oil raw materials and rational use of wastes and secondary products. One of the directions on effective use of heavy tonnage and at the same time deficit binding material as a bitumen is a wide introduction of bitumen emulsions in water into the road and civil construction practice. In addition to the advantages of bitumen, as an organic binding material, the bitumen emulsions have a number of positive properties, for example more less viscosity in the temperature interval from 0 to 100^{0}C and higher cohesion degree with a rock material surface. One of the most important quality indicators of the bitumen emulsions is their decomposition rate, in accordance with which the emulsions are classified as quick-, mid- and slow-breaking, EBC 1, 2, 3 relatively. In recent years, the most important direction of petroleum processing and petrochemistry is investigation of intensification ways of oil raw material processing and rational use of target and secondary products with optimization of their qualitative features. In solution of these problems, the tasks on development, justification of principles and processing methods, focused on obtaining of products with specified properties are highlighted. In this context, secondary products of a one-staged isoprene synthesis, which do not find rational use to the moment, are of interest. Based on the one-staged isoprene synthesis chemical composition analysis, we can suppose that its use in production of bitumen emulsions will favor to obtaining of the product with specified properties. In this connection, investigations, focused on the use of one-staged isoprene synthesis as a modifier of the bitumen emulsions, are of present interest. The paper presents experimental data on estimation of the secondary products different content effect on the bitumen emulsions' rheological properties.*

KEYWORDS: Bitumen Emulsion, Secondary Products, Properties, Modifier.

INTRODUCTION

It is known that cation bitumen emulsions (BE) were developed in the beginning of the twentieth century, and their industrial use began only in 1953, in our country. However, by a number of objective causes, they remain to be relatively new kinds of organic binding materials.

In addition to the advantages of bitumen, as an organic binding material, BE have a number of positive properties, for example more less viscosity in the temperature interval from 0 to 100^{0}C and higher cohesion degree with a rock material surface. One of the most important quality indicators of BE is their decomposition rate, in accordance with which the emulsions are classified as quick-, mid- and slow-breaking, EBC 1, 2, 3 relatively [1].

ISSN 2055-6551(Print), ISSN 2055-656X (Online)

Running characteristics, including BE decomposition rate, are regulated by introduction of modifying additives, both in a disperse phase and disperse medium. In the quality of additives in the disperse medium, stabilizers, organic and inorganic acids, polymers are usually used, this problem is studied well enough [2 – 5]. In a less degree, the effect on BE properties by different products of oil fractions is studied [6, 7]. In Russian, similar investigations, related to BE modification by the products of oil origin, were carried out in a less degree.

The most important direction of petroleum processing and petrochemistry was investigation of intensification ways of oil raw material processing and rational use of target and secondary products with optimization of their qualitative features. In solution of these problems, the tasks on development, justification of principles and processing methods, focused on obtaining of products with specified properties, on expansion of raw material base and application fields, are highlighted [8, 9]. In this context, secondary products of a one-staged isoprene synthesis (OIS), which do not find rational use to the moment, are of interest. Based on the one-staged isoprene synthesis chemical composition analysis, we can suppose that its use in BE production will favor to obtaining of the product with specified properties. In this connection, investigations, focused on OIS use as a modifier of BE, are of present interest.

MATERIALS AND METHODS

The secondary products under the investigation were obtained during a catalytic dimethyldioxan decomposition with the following isoprene separation and purification from the contact gas condensate oil layer. Their some physical-chemical characteristics are shown in Table 1.

Table 1 – Physical-chemical characteristics of the isoprene production byproducts

Indicators	Characteristics	
	OIS 1	OIS 2
Outer appearance	Oleaginous transparent liquid with a yellowish tinge	Viscous oleaginous liquid of a yellow-brown color
Density, kg/m^3	1067.00	1099.00
Acidity, % mass (in terms of ortho-phosphoric acid)	0.078	0.090
Kinematic viscosity at 50°C, mm^2/s	7.79	20.01
Flash point in an open crucible, °C	108.00	144.00

A road bitumen by BND 90/130 grade of “Ufaneftekhim” OJSC was chosen as a binding material for BE production. Currently, Tatarstan produces BE using this bitumen, which differs by a small content of straight-chain paraffin hydrocarbons (less than 2 % mass). By classification of A.S. Kolbanovskaya and V.O. Mikhailova, the bitumen under investigation belongs to the most widespread 3rd group, with the content of asphaltenes less than 25%, resins less than 36% mass, but closer to the bitumen of the 2nd group, where the asphaltenes content is less than 18%, resins – more than 36%. As is known, the bitumen of the 2nd group possesses by the best emulsifying capacity [10].

ISSN 2055-6551(Print), ISSN 2055-656X (Online)

"Dinoram SL" by "CECA" company, a cation-active surfactant, based on a fat polyamine, was used in our investigations as an emulsifier. Dependence of the surface tension at the boundary the bitumen solution in CCl_4 – water from the emulsifier concentration in the water phase at temperature in 20^0C is presented on Figure 1.

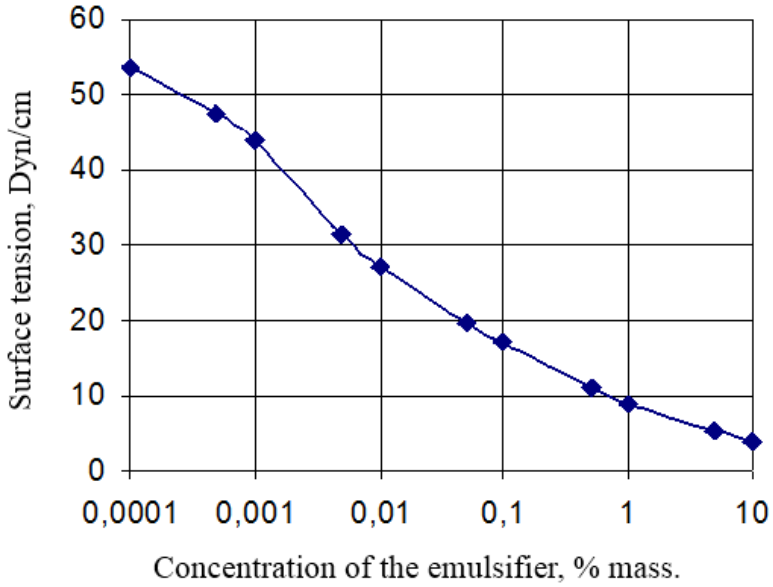

Figure 1 – Dependence of the surface tension on the emulsifier concentration

As follows from the presented dependence, the surface tension decreases exponentially with increase in the emulsifier concentration. Formation of the emulsions is possible at the surface tension decrease in less than 20 Dyn/cm [3]. Thus, the bitumen emulsion formation is possible at the emulsifier concentration more than 0.1 % mass.

RESULTS AND DISCUSSION

BE with the content of water and bitumen phase in equal proportions by 50 % mass relatively were prepared at the research. OIS quantity changed from 0.5 to 10 % mass. Further increase in OIS concentration was of no interest owing to its premature breakdown. As the research results show, OIS differential peculiarity is its ambiguous influence on the bitumen emulsions' composition and properties (Table 2).

It should be noted that in the national technical standard, the emulsions' breakdown rate is determined qualitatively, by miscibility with a mineral part of different porosity [1]. To estimate the breakdown rate, we used a quantitative characteristic, called a breakdown index (BI) – relation of the sand quantity (g) used for the breakdown of 100 g of the emulsion. It is commonly supposed that this value has dimension g/100g [11].

BI maximal values were observed at OIS content from 0.5 to 2 % mass. BI similar dependence on OIS content was also observed for the emulsifier in amount of 0.25 % mass, i.e. BI extreme values were observed for OIS with the content in 0.5 – 2 % mass. BI obtained values from OIS content independently on the emulsifier amount are indicative of OIS general influence

ISSN 2055-6551(Print), ISSN 2055-656X (Online)

mechanism on the emulsions' properties, as with increase in OIS content, BI decreases independently on the introduced emulsifier amount.

It should be noted that in OIS introduction in more than 7 % mass, independently on the emulsifier amount, there is the emulsions' premature breakdown. The authors link such phenomenon with the fact that functional, reactive groups of OIS form stable complexes with the emulsions' bitumen phase, in consequence of which, further coagulation occurs.

The emulsions' relative viscosity also depends on the amount of introduced OIS and has the same extreme character as BI. In this case, independently on the emulsifier amount, increase in the relative viscosity was observed in OIS content in 5 – 7 % mass.

Table 2 – Qualitative characteristics of the bitumen emulsions with OIS participation

Sample number	Quantity, % mass		Breakdown index, g/100g		Relative viscosity, c		Adhesion, points	
	OIS	Emulsifier	OIS 1	OIS 2	OIS 1	OIS 2	OIS 1	OIS 2
1	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
1	0,5	0,5	390.0	329,2	23.0	23,8	4-5	4.0
2	1.0	0,5	380.0	322,5	21.0	18,9	5.0	4.0
3	2.0	0,5	320,40	318,2	21,9	21.0	4.0	5.0
4	3.0	0,5	313,05	315,7	23,4	23,6	4.0	4.0
5	4.0	0,5	307,80	312,6	24,2	25,5	3.0	3.0
6	5.0	0,5	295,35	309,32	27.0	26,2	3.0	3.0
7	6.0	0,5	287,4	306,7	25,3	24	3.0	3.0
8	7.0	0,5	280.0	305,2	23,8	22,6	3.0	3.0
9	8.0	0,5	Broken		-		-	
10	9.0	0,5	« «		-		-	
11	10.0	0,5	« «		-		-	
12	-	0,5	482,50		26,4		2	
13	0,5	0,25	337,8	353.0	21,4	28,7	5.0	4.0
14	1.0	0,25	319,15	335,95	19,6	17,4	4.0	5.0
15	2.0	0,25	312,20	327,4	20,4	19,6	4.0	4.0
16	3.0	0,25	305,10	322,6	21,8	22.0	3.0	4.0
17	4.0	0,25	301,26	314,25	22,6	24.0	3.0	3.0
18	5.0	0,25	293,70	300,1	25,6	25	3.0	3.0
19	6.0	0,25	289,81	275.0	23,4	27,1	3.0	3.0
20	7.0	0,25	286,2	250.0	20.0	29.0	3.0	3.0
21	8.0	0,25	Broken		-		-	
22	9.0	0,25	« «		-		-	
23	10.0	0,25	« «		-		-	
24	-	0,25	460.0		24.0		2.0	

Further investigations were focused on the study of the secondary products' influence on the bitumen emulsions' adhesive properties. Analysis of the obtained data testifies that the maximal adhesion values have samples with OIS content from 0.5 to 3 % mass. independently on the emulsifier content in the system. This allows plan decrease in the emulsifier amount, as

ISSN 2055-6551(Print), ISSN 2055-656X (Online)

an expensive component, which part's reduction will result both in improvement of the emulsions' properties and their significant cheapening. OIS introduction causes the bitumen properties' change, as well as change in the thickness of the bitumen particle complex structural unit adsorptive-solvate layer in the emulsions, which high-molecular compounds adsorb in the bitumen droplets' adsorptive-solvate layer. When OIS concentration is exceeded in more than 7 % mass., there is coagulation and sedimentation of the bitumen phase.

With a view of more detailed study of OIS fractional composition influence on the bitumen emulsions' main characteristics, the products of isoprene synthesis were exposed to the atmospheric distillation at the residual pressure in 15 mm hg with a view of the following separation on 10 – 15 % narrow fractions. The obtained data are presented in Table 3.

Table 3 – Results of the secondary products' fractional distillation

Final boiling point of the factions, ^{0}C		Fractional composition, % mass
1	2	3
OIS 1.1	Below the critical – 75	12,65
OIS 1.2	75-90	7,97
OIS 1.3	90-110	2,91
OIS 1.4	110-120	7,08
OIS 1.5	120-135	50,63
OIS 1.6	135-160	18,76
Distillation residue		Completely distilled
OIS 2.1	н.к.-140	8,36
OIS 2.2	140-155	23,3
OIS 2.3	155-170	5,42
OIS 2.4	170-185	11,55
OIS 2.5	185-200	9,16
OIS 2.6	200-215	11,15
OIS 2.7	215-240	18,71
OIS 2.8	Distillation residue	12,35

The evolved narrow fractions, as well as undistilled residue, were tested as additives to the emulsions, at the same conditions that OIS before the fractionation. It should be noted that the studied fractions were introduced in the emulsions in the quantities comparable with the content of the fraction in the initial OIS. Results of the investigations using samples OIS 1 and OIS 2 with different boiling point temperature are shown on Figures 2 – 7.

Depending of OIS fraction and quantity introduced, the emulsions had different stability, viscosity and breakdown index. With the light fraction sampling depth, the emulsions with participation of weighted OIS part behave themselves ambiguously, however, they all had more lower BI than emulsions without OIS participation.

It follows from the results presented on Figures 2 and 3 that BI dependences on the concentration for addition of fractions OIS 1.1 and OIS 1.2, as well as OIS 2.1, 2.3 – 2.7 are characterized as steadily decreasing with increase in their concentration.

ISSN 2055-6551(Print), ISSN 2055-656X (Online)

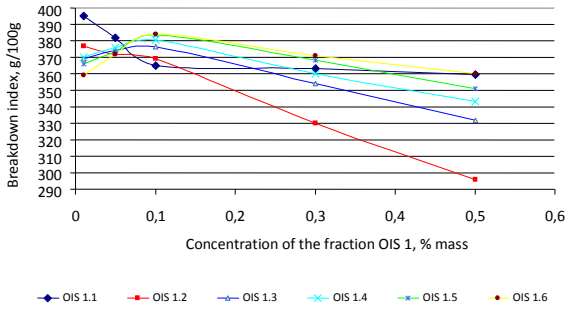

Figure 2 – Dependences of WBE breakdown index change on OIS 1 fractions' concentration

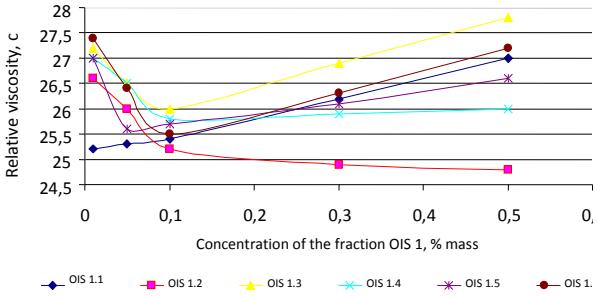

Figure 5 – Dependences of WBE relative viscosity change on OIS 1 fractions' concentration

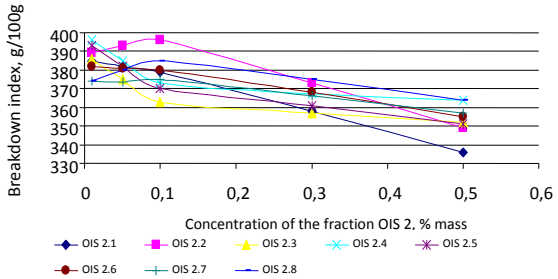

Figure 3 – Dependences of WBE breakdown index change on OIS 2 fractions' concentration

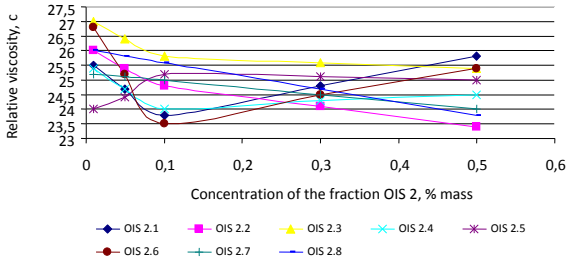

Figure 6 – Dependences of WBE relative viscosity change on OIS 2 fractions' concentration

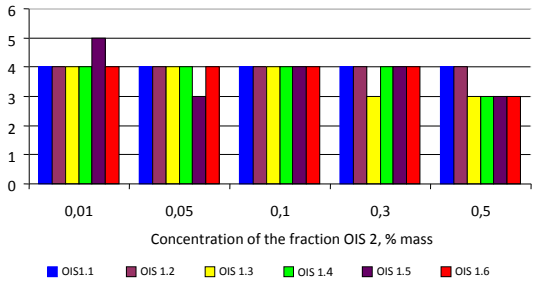

Figure 4 – Dependences of WBE adhesion change on OIS 1 fractions' concentration

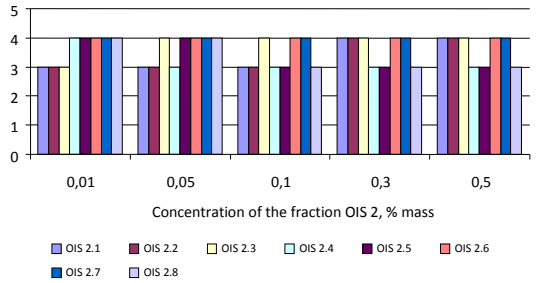

Figure 7 – Dependences of WBE adhesion change on OIS 2 fractions' concentration

Together with that, the obtained dependences with addition of the fractions OIS 1.3 – 1.6, OIS 2.2 and 2.8 bear an extreme character with the maximum at the additive concentration in 0.1 % mass. It can be supposed that compounds in the fractions favor to BI increase. In general,

ISSN 2055-6551(Print), ISSN 2055-656X (Online)

the obtained dependences of the breakdown index on the concentration of OIS fractions introduced are indicative of the general action character of the fraction on the emulsions' properties.

As for the emulsions' relative viscosity, it also depends on the concentration of OIS fractions introduced in the most cases with the extreme character. The relative viscosity minimal value is observed at introduction of OIS 1.3, 1.4, 1.6, 2.1, 2.4, 2.6 at the concentration in 0.1 % mass., as well as in introduction of the fraction OIS 1.5 in amount of 0.05 % mass. All other dependences of the relative viscosity on the introduced fractions' concentration are characterized as steadily decreasing, except for one dependence (the relative viscosity increases with increase in the concentration of OIS 1.1 fraction).

Interesting data on the influence of evolved fractions of the emulsions' properties are observed for the adhesion, especially for OIS 2. Analysis of the data testifies that with increase in the concentration of OIS 2.1 – 2.3, 2.6 and 2.7 fractions, the adhesion increases.

The conducted investigations allowed us suppose that compounds increasing BI, improving the adhesion, are presented not only in any or some fractions, but also about more complex action of many OIS components on the bitumen emulsions' qualitative characteristics.

CONCLUSIONS

Thus, the optimal OIS concentrations in the bitumen emulsions with a view to improve their qualitative characteristics, reduce consumption of the expensive emulsifier, and thereby significantly improve technical-economic indicators of the production, were determined in the course of the conducted investigations. Also, the interaction between physical-chemical properties of the bitumen and OIS concentrations in the bitumen emulsions was established. It was demonstrated that at the introduction of OIS additives in the emulsion, there is increase in the working time interval of the binding material plasticity and in improvement of its adhesive properties.

REFERENCES

State Standard 52128-2003. Road bitumen emulsions. Specifications. – Intr. October 1, 2003. – 22 p. (in Russian)

Karpeko F.V. Bitumnye emulsii. Osnovy fiziko-khimicheskoy tekhnologii proizvodstva i primeneniya. [Bitumen emulsions. Fundamentals of physical-chemical technology of production and application.] / F.V. Karpeko, A.A. Gureyev. – M.: TSNIITEneftekhim, 1998. – 192 p.

Kuchma M.I. PAV v dorozhnom stroitelstve [Surfactants in the road building] / M.I. Kuchma. – M.: Transport, 1980. – 192 p.

Kemalov R.A., Glady E.A., Kemalov A.F. Modifitsirovannye vodobitumnye emulsii [Modified water-bitumen emulsions]. *Materialy konferentsii "Perspectivy razvitiya khimicheskoy pererabotki goryuchikh iskopayemykh"* [Materials of conference "Prospects for the development of chemical processing of inflammable minerals". Saint-Petersburg: KHIMIZDAT 2006. – P. 189. (in Russian)

ISSN 2055-6551(Print), ISSN 2055-656X (Online)

Kemalov R.A., Glady E.A., Kemalov A.F. Poluchenie bitumnoi emulsii na osnove emulgatora s dobavkoi [Production of a bitumen emulsions on the base of an emulsifier with an additive]. *Materialy Mezhdunarodnoi nauchno-prakticheskoi konferentsii "Neftegasopererabotka i neftekhimiya – 2006"* [Materials of International scientific-practical conference "Oil-gas-processing and petrochemistry – 2006"]. Ufa, 2006. – P. 110. (in Russian)

Patent US 4.211.575, Int. cl. C 08 L 95/00; C 09 D 3/24. Asphalt-sulfur emulsion composition. – Jur. 8, 1980.

Patent US 4.282.037, Int. cl. C 08 L 95/00; C 09 D 3/24. Galsonite emulsion composition. – Aug. 4, 1981.

Glady E.A. *Vtorichnye produkty proizvodstva izoprena v kachestve modifikatorov bitumnykh emulsii.* Avtoreferat diss. cand. tekh. nauk [Secondary products of isoprene production as modifiers of bitumen emulsions. Cand.eng.sci.diss.abst.]. Kazan, 2009. 20 p.

Kemalov A.F. *Intensifikatsiya proizvodstva okislennykh bitumov i modifitsirovannye bitumnye materialy na ih osnove.* Avtoreferat diss. Dr. tekh. nauk [Intensification of air-rectified bitumen and modified bitumen materials on their base. Dr.eng.diss.]. Kazan, 2005.

Kolbanovskaya A.S. Optimal'naya struktura bituma v asfal'tovom betone [Optimal bitumen structure in an asphaltic concrete]. *Materialy rabot simposiuma po structure i strukturoobrazovanii v asfal'tobetone* [Materials of papers of a symposium on the structure and structure formation in a bituminous concrete]. Soyuzdornii, 1968. – PP. 12-19. (in Russian)

Petukhov I.N. Dorozhnye emulsii [Road emulsions] / I.N. Petukhov. – Minsk: EADE, 1997. – 230 p.

ISSN 2055-6551(Print), ISSN 2055-656X (Online)