

Bitumen Modified by Phenol-Cresol-Formaldehyde Resins Obtained From Coking By-products

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Abstract – Resins were synthesized via phenol polycondensation with formaldehyde from the coal coking by-product, phenol fraction namely. Phenol-cresol-formaldehyde resins were obtained from the fractions b.b.-185 °C (PhCFR-1) and “raw” phenol obtained from the fraction b.b.-185 °C (PhCFR-2). It was established that the resulting resins may be used as modifiers of road bitumen.

Keywords – modified bitumen, «raw» phenol, phenol-cresol-formaldehyde resin.

I. Introduction

Approximately 85% of oil bitumen is used as an astringent in the ways of asphalt stacking: pavements, highways, airports etc. It's a basic binding agent that is used for highway engineering. There are some difficulties in using of the road bitumen, but the most essential problem is that the adhesion properties of the bitumen commodities are not high enough (even if it meets the requirements of the normative documents) [1].

One of the ways of the problem solution is the modification of the commercial road bitumen. For road bitumen modification usually are used the block copolymers of styrene SBS type, it is caused not only its ability to improve the bitumen strength but also to provide a polymer-bitumen elastic compositions, even in a low temperature [2-4].

The main drawback is high price, what moderates the growth rate of modified by the thermoelastoplasts bitumen (price is higher in 1,5-2,5 times rather than non modified [5]).

It is important to find inexpensive substances which improve the operating characteristics of bitumen, first of all adhesive.

The experiments of getting relatively cheaper and effective oil bitumen modifiers from the by-products of coking coal are conducted at the department of Chemical Technology of oil and gas processing, Lviv Polytechnic National University [6-8].

It is known [2-4], while modifying the oil bitumen quite effective modifiers are phenol-formaldehyde resins. But resins got from the phenol, is not widely used as polymer modifiers because of its high price. On the other hand, one of the coke-chemical enterprises products is phenol fraction with the output of 1,5 – 2,5 % wt on fresh coal, there is a considerable part of phenol and cresol (around 65 %) form in the coking process. The cost of the coal tar

phenol fraction contains 35-50% wt of the phenol, it is in 35-40 times lower than cost of the synthetic phenol [9]. The purpose of the experiments was to show the possibility of the oil bitumen modification by the phenol-formaldehyde resins, got from the by-products of the coking coal process

II. Experimental

The phenol fraction was used for synthesis, selected on JSC Zaporizhko.

The scheme of experiments performing is in the fig.1. In order to separate phenol and cresols mixtures was performed the distillation of phenol fraction on two fractions – b.b. fraction – 185 and 185-e.b. fraction °C (the temperature of phenol boiling is 182 °C, cresols – 191-202 °C). Then from the b.b. fr. – 185 °C the phenol was concentrated («raw» phenol was got). The phenol disengagement from the b.b. fr.-185°C was performed by 10% NaOH solution, with phenol it forms water soluble phenolates, conversion into phenol was made by the concentrated hydrochloric acid. (Fig.1)

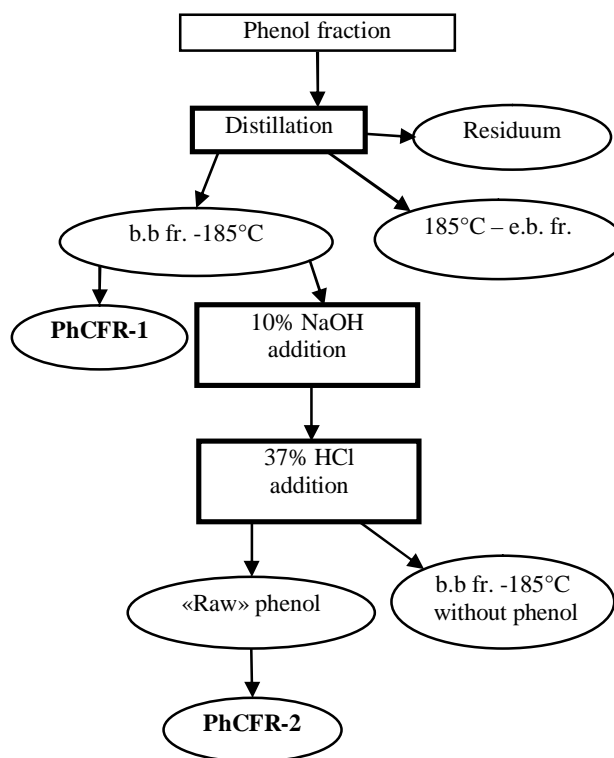


Fig.1 Scheme of research.

The material balance of distillation is given in the Table 1

TABLE 1

THE MATERIAL BALANCE OF PHENOL FRACTION DISTILLATION

Article / Value	fresh, % wt
b. b.fr. -185 °C (phenol concentrate)	50,60
fr. 185-e. b. °C (cresol concentrate)	46,77
Residuum	2,63
Total	100,00

The method of phenol polycondensation with formaldehyde was used to synthesize resins from the b.b. fraction. -185 °C (PhCFR-1). The yield of «raw» phenol is 28,8 % wt for b.b.fr. -185 °C.

III. Result

The conditions of PhCFR-1 and PhCFR-2 are in the Table 2 [10].

TABLE 2

THE CONDITIONS OF PHENOL – FORMALDEHYDE RESINS SYNTHESIS

Parameter	Value
Molar relation phenol / formaldehyde	1,42
Catalyst content (conc. HCl), % wt on phenol	0,1
Temperature, °C	100
Process duration, min.	60

The yields of the resins are in the Table 3.

TABLE 3

THE YIELDS OF PHENOL – CRESOL – FORMALDEHYDE RESINS

Resin	b.b. fr.-185, % wt
PhCFR-1	24,3
PhCFR-2	26,1

The oil bitumen was modified at 110 and 190 °C by the phenol-formaldehyde resins. The characteristics of the bitumen-polymer mixtures are in the Table 4.

TABLE 4

THE CONDITIONS OF PREPARING AND CHARACTERISTICS OF BITUMEN MODIFIED BY THE POLYMER

Indicators	Output bitumen	Modification temperature, °C			
		2,5 % wt PhCFR-1 the bitumen output		2,5 % wt PhCFR-2 the bitumen output	
		110	190	110	190
Softening temperature (ball & ring method) (°C)	45	48	48	–	48
Penetration at 25 °C (0,1 mm)	67	62	42	–	52
Ductility at 25 °C (cm)	>90	>90	>90	–	>90
Adhesion to glass (%)	49,5	90,2	87,4	–	94,5
Homogeneity	+	+	+	non-homogeneous	+

Conclusion

Compare the data given in the table 4, it is clear that loading into bitumen phenol-formaldehyde resins – 2,5% wt, increases the melting temperature and adhesion of oil bitumen. Modification of PhCFR-1 of oil bitumen should be conducted at 110 °C, because at 190 °C the modified bitumen becomes less plastic; phenol-formaldehyde resins 2 – at 190°C, because at 110 °C it is modified bitumen what doesn't meet the requirements of homogeneity.

Also the results show (Table 3) the yield of of phenol PhCFR-2 is much higher than PhCFR-1. So, it is more expedient to get the phenol-formaldehyde resins from «raw» phenol.

References

- [1] Anonymous, Second edition 2011, "The Bitumen Industry". Available: <http://www.bitumenuk.com/images/library/files/Bitumen%20Industry/TheBitumenIndustryMarch2011Edition.pdf>.
- [2] V. Haldina, "Modifitsyrovanye bitumy: rukovodstvo" p. 228, 2009.
- [3] Z. Jiqing, B. Birgisson, N. Kringos, «Polymer modification of bitumen: Advance and challenges», European Polymer Journal, vol. 54, pp. 18-38, 2014.
- [4] R. Tarasov, V. Makarova, A. Kadomtseva, "Modyfikatsya bitumov polimeramy, Sovremennye nauchnye isledovaniya i innovatsii", vol.5, 2014. Available:<http://web.snauka.ru/issues/2014/05/34687>.
- [5] S. Krischynskiy, "Physical and chemical properties of bitumen, modified, modified by the complex modifier Polyd", Vestn. KhNADU, vol. 40, pp. 28-32, 2008.
- [6] S. Pyshyev, Yu. Grytsenko, H. Bilushchak, R. Pyshyeva, N. Danyliv, "Production of Indene-coumarone Resins as Bitumen Modifiers, Petroleum and Coal", vol. 57, pp. 303-324, 2015.
- [7] S. Pyshiev, J. Hrytsenko, Y. Khlibnyk, H. Strap, T. Koval, "Influence the polimer nature on the properties of the modified bitumen", Eastern European Magazine of Advanced Technology, vol. 68, pp. 4-8, 2014.
- [8] S. Pyshiev, J. Hrytsenko, I. Nikolysyn, Z. Hnativ, "Preparation of indene-coumarone resins for the modification of oil road bitumen", Carbon chemistry magazine, vol. 5, pp. 41-48, 2014.
- [9] T. Hoholeva, V. Shustikov, «Chemistry and technology of coal tar processing», p. 256, 1992.
- [10] A. Toroptseva, K. Belohorodskay, V. Bondarenko, "Laboratory practicum on chemistry and technology of high-molecular compounds", pp. 199-200, 1972