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«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ  
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»  
АКЦИОНЕРЛІК ҚОҒАМЫ

# ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

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## ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

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S. S. KOZHABEKOV, A. A. ZHUBANOV, T. ZHEXENBEK

Kazakh-British Technical University, Almaty, Republic of Kazakhstan

## MODIFIED ETHYLENE-VINYL ACETATE COPOLYMER AS A DEPRESSANT OF POUR POINT WAX OIL

**Abstract.** The ethylene–vinyl acetate copolymer (EVA) was modified by hydrolysis of acetate groups. The separately hydrolysed copolymer was characterized by Fourier transform infrared spectroscopy (FTIR). Research was carried out to determine the influence of modified EVA polar groups on decrease the pour point temperature of oil. The results showed that EVA greatly decrease the Pour Point Temperature (PPT) of paraffin oil. In addition, EVA with strong polarity could provide greater electrostatic repulsion force to wax crystals, which made the wax crystals have more difficulty to connect together and form a much looser network structure.

**Key words:** Pour Point Depressant (PPD), ethylene–vinyl acetate copolymer (EVA), modified copolymer, wax.

**Introduction.** Nowadays oil and gas industry undergoes significant financial expenses and technical and technological difficulties due to the current trend of increasing content of heavy and viscous oil. Those abnormal rheological properties that are mainly introduced as high viscosity and high temperature of solidification correspond to oil from Kazakhstan's oil fields (deposits of Mangyshlak Peninsula, Akshabulak and other regions). Almost all types of oil in Kazakhstan can be classified as waxy, solidifying at positive temperatures, and high viscous oil. In particular, viscosity of high viscous oil even under normal conditions fluctuates in the range of several hundred, and sometimes thousands of centipoises [1-3].

Wax deposition are both a down hole and topside problem blocking the flow of hydrocarbons fluids as they are cooled [4].

Wax deposition is one of the major flow assurance risks and it should be considered during the transportation of heavy, waxy and high viscous crude oil. Flow assurance risks including wax deposition and wax gelation become a bigger concern for oil transportation sector [5].

Therefore, an important issue is to synthesize or modify polymeric depressants that will provide the improvement of rheological characteristics of waxy and high viscous oil that present in Kazakhstan's oil fields. The key role played by this additive is co-crystallizing with the paraffin existent in oil, promoting the highest possible disarrangement of wax crystallization process [6].

In this study, ethylene–vinyl acetate copolymer (EVA) was modified by alkali-catalyzed alcoholysis and investigated the properties of the resulted copolymer into pour point depressant of crude oil.

## EXPERIMENTAL PART

## Materials and methods

**Characteristic of initial reagents.** Poly (ethylene-co-vinyl acetate) with the content of vinyl acetate monomeric unit of 25 wt.% and exhibiting melt flow indices of 19 g/min produced by "Sigma-Aldrich Chemicals GmbH" was used without further purification.

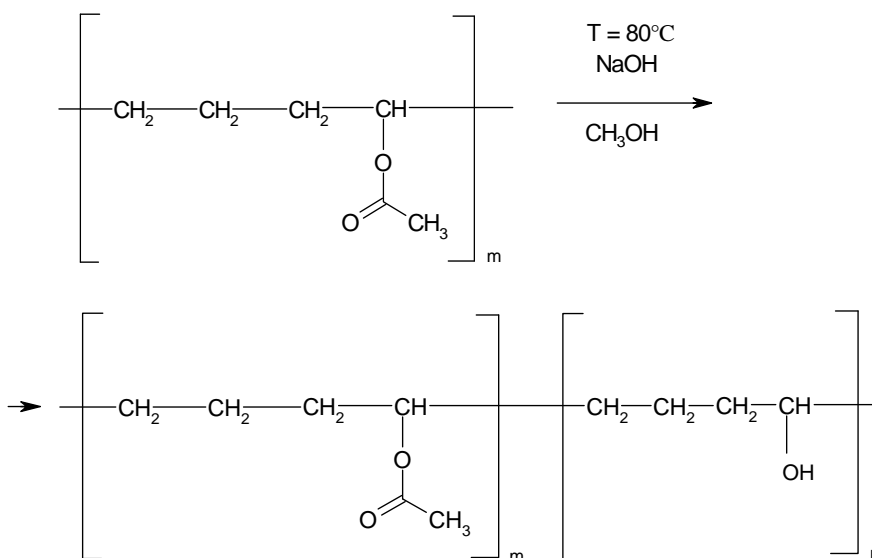
Methanol produced from "Sigma-Aldrich Chemicals GmbH" was used without further purification.

Sodium hydroxide from "Sigma-Aldrich Chemicals GmbH" was used without further purification.

Toluene was used as an organic solvent for the reaction of hydrolysis. The purification of toluene was performed according to standard procedures. The density is 0.865 g/mL at 25°C and boiling point is 110-111°C. The vapor point is equal to 26 mm Hg (25°C).

Depressant additive DMN-2005 of company "DEPRAN" (Russia) was used without further purification.

**Procedure of modification of ethylene-co-vinyl acetate polymers with base.** In a three-necked round bottom flask fitted with a reflux condenser (Dean-Stark apparatus), a thermometer, a magnetic stirrer, 2.0 g of EVA copolymer (containing vinyl acetate groups 25% wt.) was dissolved in 30 ml of toluene. After that, 1 mL of 2% solution of sodium hydroxide in methanol was added to the solution of the copolymer. Partial hydrolysis reaction proceeds according to the following scheme [6]:



The reaction was refluxed at 80°C during predetermined period equal to 30 minutes. Sodium hydroxide solution was neutralized with alcoholic solution of hydrochloric acid. Then, inorganic layer was eliminated, the polymer (organic) layer was reprecipitated into methanol, filtered and dried in vacuum at 50°C until constant weight. Under these conditions the modified EVA copolymer obtained hydrolysis degree of 5 mol. % (related to acetate moieties).

**Determination of the Pour Point of wax oil.** The methodology used for the assessment of the oil pour points was based on an adaptation of the ASTM Method 5853. The cooling bath was equipped with two thermostats: LAUDA RE-415 that maintains the temperature of 0°C, LAUDA RE-210 that maintains the temperature of -17°C.

## RESULTS AND DISCUSSION

**Modification of ethylene-co-vinyl acetate copolymers with bases.** Modification of ethylene-co-vinyl acetate copolymers with sodium hydroxide solution was carried out in the conformity with standard procedures of partial hydrolysis. The results of the reaction can be detected through the application of different methods of examination. The degree of hydrolysis and the yield of the modification reaction were investigated by means of FTIR-spectroscopy of obtained products. Below the spectrums of initial agents and products are described.

Figure 1 shows the FTIR spectrum of EVA copolymer. Characteristic absorption bands of the copolymer EVA are in:

- 1735  $\text{cm}^{-1}$ , corresponding to the absorption of the stretching vibrations of C = O carbonyl group in esters;
- 2915 and 2847  $\text{cm}^{-1}$ , relating to the absorption of the stretching vibrations of  $\text{CH}_3$  groups and  $-\text{CH}_3-\text{CH}_2$ -ester groups.

Figure 2 represents the FTIR spectrum of partially hydrolyzed ethylene-vinyl acetate copolymer (degree of hydrolysis - 5%). There are a reduction of band intensity in the range of 1735-1738  $\text{cm}^{-1}$  - stretching vibrations of the carbonyl group  $-\text{C}=\text{O}$  in esters and an appearance in the spectrum of the hydrolyzed EVA of a wide absorption band of 3236  $\text{cm}^{-1}$ , corresponded to the stretching vibrations of the  $-\text{OH}$  group.

Moreover, a reduction of the intensity of the absorption bands in the 2915 and 2847  $\text{cm}^{-1}$ , related to the absorption of the stretching vibrations of  $\text{CH}_3$ - groups and  $-\text{CH}_3-\text{CH}_2$ -ester groups, and a strong reduction in the intensity of the absorption band of 1236  $\text{cm}^{-1}$  in the spectrum of the initial EVA, corresponded to absorption band of fluctuations with regard C-O group in acetate are observed.

Above-mentioned absorption band is absent in the spectrum of the completely hydrolyzed EVA that is presented on Figure 3.3 and it indicates a complete hydrolysis of ethylene-co-vinyl acetate. On the evidence of this: there is the almost a complete reduction in the intensity of the absorption bands observed in 2915 and 2847  $\text{cm}^{-1}$  relating to the absorption of the stretching vibrations of  $-\text{CH}_3$  groups and  $-\text{CH}_3-\text{CH}_2$ -ether groups. In addition, there is an almost a complete

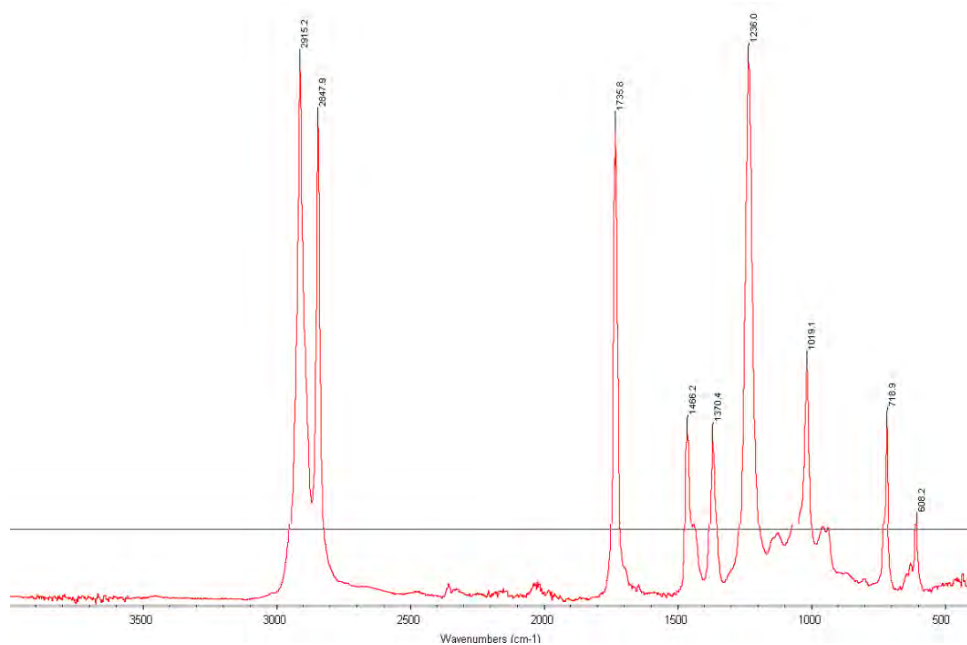


Figure 1 – FTIR spectrum of EVA copolymer

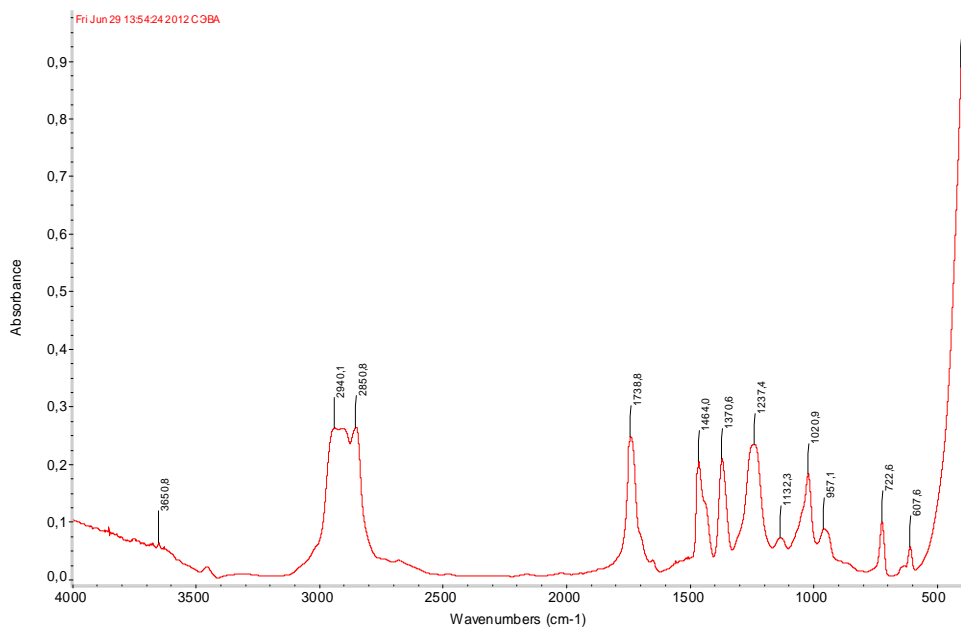


Figure 2 – FTIR spectrum of partially hydrolyzed EVA copolymer (hydrolysis degree – 5%)

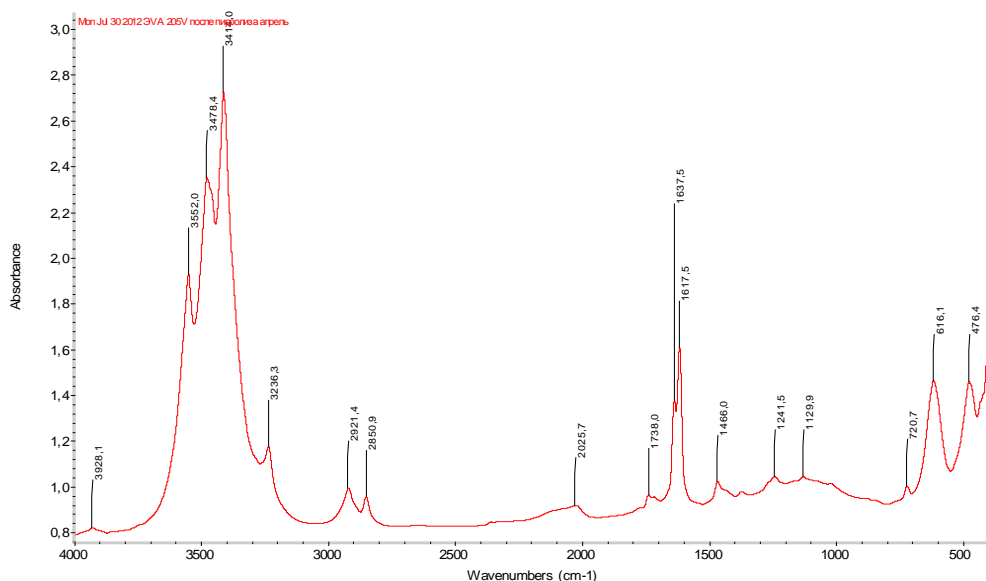


Figure 3 – FTIR spectrum of completely hydrolyzed EVA

absence of bands in the 1735-1738  $\text{cm}^{-1}$  - stretching vibrations of the carbonyl group  $\text{C} = \text{O}$  in esters, the presence of a broad absorption band of 3236  $\text{cm}^{-1}$  corresponding to the stretching vibrations of  $-\text{OH}$  groups [7].

Table 1 – General physical, chemical and rheological characteristics of oils of oil fields in the South Turgay basin [8]

№	Crudeoil	$d_4^{20}$ , $\text{kg/m}^3$	WAT $^{\circ}\text{C}$	Wax, %	Asphalt., %	Resins, %	Fraction, %		
							200 $^{\circ}\text{C}$	300 $^{\circ}\text{C}$	350 $^{\circ}\text{C}$
1	Kumkol'	810,4	12	14,4	0,1	7,6	29	49	59
2	Akshabulak	829,7	21	14,3	0,6	8,6	29	48	58
3	Konys	874,4	24	16,5	2,0	7,1	15	33	47
4	Bektas	825,7	21	19,4	1,2	9,6	29	48	58
5	Aschysay	878,2	21	20,1	1,3	9,2	20	39	51

**Effect on wax appearance temperature of waxy crude oils.** The pour point depressant that was injected into oil disperse system modifies formed crystals of paraffin and regulates the structure of oil dispersion by means of increasing its aggregative stability. Therefore, a certain pour point corresponds to determined oil type with certain injected depressant additive. According to the results of experimental tests on determination of wax appearance temperature, conclusions on the influence of modified pour point additives have been done.

The key point is the impact of additives on the pour point depression and cloud point depression for different types of oil and oil mixtures. Compared to the

original ethylene-vinyl acetate copolymer, the chemical structure of modified EVA displays more polarity due to the presence of hydroxyl groups, which promote better disarrangement during wax crystallization process. The lack of paraffinic chains in the structure of partially hydrolyzed EVA is one of the reasons of better results achieved by modified EVA copolymers [7].

Table 2 shows wax appearance temperature change of crude oils and oil mixtures when heat-treated and treated with additives. As it can be seen from the table, modified additive has high performance and this magnitude is stable for different types of oil.

Table 2 – Wax appearance temperature of waxy crude oils in the South Turgay basin after heat and additive treatments

Waxy crude oil	Treatment	Pour Point, °C
Akshabulak	Heat treatment	+18
	Industrial additive	+6
	Modified EVA	0
Achysay	Heat treatment	+21
	Industrial additive	+15
	Modified EVA	+9
Konys-Bektas	Heat treatment	+24
	Industrial additive	+12
	Modified EVA	+6
Kumkol	Heat treatment	+12
	Industrial additive	0
	Modified EVA	-3

**Conclusion.** Modified a new ethylene–vinyl acetate copolymer (EVA) with alcohol in presence of sodium hydroxide. The alcoholized copolymer was characterized by Fourier transform infrared (FTIR) spectroscopy. The obtained copolymer was tested into pour point depressant (PPD) of crude oil of different crude oils from different oil basin. The results showed that EVA greatly decreases the Pour Point of crude oil compared to industrial additives and heat treatment.

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### Резюме

*С. С. Кожобеков, Ә. Ә. Жубанов, Т. Жексенбек*

#### ЭТИЛЕН-ВИНИЛАЦЕТАТТЫҢ ТҮРЛЕНДІРІЛГЕН СОПОЛИМЕРІН ПАРАФИНДІ МҰНАЙДЫҢ ҚАТУ ТЕМПЕРАТУРАСЫН ТӨМЕНДЕТУДЕ ҚОЛДАНУ

Этилен және винилацетаттың сополимері (ЭВА) ацетаттық топтың гидролизі арқылы түрлендірілді. Ішінара гидролизденген сополимер инфрақызыл Фурье спектроскопиясы (FTIR) арқылы сипатталды. ЭВА түрлендірілген полярлы тобының, мұнайдың аққыштығын жоғалту температурасының төмендетуіне әсері зерттелді. Нәтижесінде ЭВА парафинді мұнайдың аққыштығын жоғалту температурасын едәуір төмендететіні анықталды. ЭВА сополимері түрлендіруден кейін парафин кристалдарын үлкен электростатикалық тебіліс күшімен қамтамасыз етеді және де әлсіз байланысқан парафин кристал торларының қалыптасуына жағдай жасайды.

**Түйін сөздер:** аққыштық температурасын төмендету қоспасы, этилен және винилацетаттың түрлендірілген сополимері (ЭВА), парафин.

### Резюме

*С. С. Кожобеков, А. А. Жубанов, Т. Жексенбек*

#### МОДИФИЦИРОВАННЫЙ СОПОЛИМЕР ЭТИЛЕН-ВИНИЛАЦЕТАТ КАК ДЕПРЕССАНТ ТЕМПЕРАТУРЫ ПОТЕРИ ТЕКУЧЕСТИ ПАРАФИНИСТОЙ НЕФТИ

Модифицирован сополимер этилена и винилацетата (ЭВА) путем гидролиза ацетатной группы. Частично гидролизованный сополимер изучали инфракрасной Фурье спектроскопией (FTIR). Исследовано влияние модифицированных полярных групп ЭВА на снижение температуры потери текучести нефти. Результаты показали, что ЭВА значительно снижает температуру потери текучести (ТПП) парафинистой нефти. Сополимер ЭВА после модификации может обеспечить большую электростатическую силу отталкивания кристаллов парафина, и создает условия для формирования гораздо более слабосвязанной кристаллической сетки парафинов.

**Ключевые слова:** депрессант температуры потери текучести (PPD), модифицированный сополимер этилена и винилацетата (ЭВА), парафин.