

## DEVELOPMENT OF EFFECTIVE ADDITIVE MATERIALS FOR LUBRICANTS FROM SECONDARY RESOURCES

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### Abstract:

In the article are considered some questions of the creation new and hither efficient additive anticorrosion and depression of the action on base available and cheap raw materials resource. They are determined main practical features additive, are revealed kinetic regularities and mechanisms anticorrosion protection of the metallic details of the machines and designs. The chemical stability of lubricant defined the oxidation an probing them in bomb under pressure of the oxygen (8 atm) under 100oC or bore the probing in special ditch in thermostats under raised to temperature. About stabilities judged on the amount of the absorbed oxygen, at time and on growth acid number lubricant. It is installed that introduction designed additive in composition of lubricant brings about reduction of water, in consequence of hydrophylling compositions that also reduces the corrosion of the metallic parts mechanism.

**Keywords:** Additive, anticorrosion protection, syntheses, mechanism, depressor, cheese, resource, rheological, kinetics, velocity, viscosity.

### РАЗРАБОТКА ЭФФЕКТИВНЫХ ПРИСАДОЧНЫХ МАТЕРИАЛОВ К СМАЗКАМ ИЗ ВТОРИЧНЫХ РЕСУРСОВ

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### Аннотация:

Мақолада маҳаллий арзон ва қулай хом-ашёлар, жумладан ёғ-мой саноати чиқиндилари асосида юқори эффектли коррозияга чидамли ва депрессор янги қўндирмаларни яратишнинг баъзи бир саволлари кўриб чиқилган. Машиналарнинг металл деталлари ва конструкциялари коррозияга чидамлилигини ошириш ва ундан ҳимояланишнинг кинетик



қонуниятлари, механизмлари ҳамда қўндирмаларнинг асосий амалий характеристикалари аниқланди. Сурков мойларининг кимёвий стабиллигини уларни бомбанинг ичида кислороднинг 100°C (8 атм/босими ости)да ёки навескани термостатда махсус кювета ичида юқори ҳароратда ушлаб туриш орқали аниқланди. Вақт оралиғида ютилаётган кислород ва кислота сонининг ортиши миқдorigа қараб унинг стабиллиги ҳақида хулоса қилинди. Ишлаб чиқилган қўндирмаларни сурков мойлари таркибига киритилганда сувнинг камайиши композициянинг гидрофиллиги самараси бўлиб, у шу билан бирга металл механизми қисмларининг коррозияланишини ҳам камайтиради.

## **Аннотация:**

В статье рассмотрены некоторые вопросы создания новых и высокоэффективных присадок антикоррозионного и депрессорного действия на основе доступных и дешевых сырьевых ресурсов, а именно, из отходов масложировой промышленности. Определены основные практические характеристики присадок, выявлены кинетические закономерности и механизмы антикоррозионной защиты металлических деталей машин и конструкции. Химическую стабильность смазок определяли окислением навески их в бомбе под давлением кислорода (8 атм) при 100°C или выдерживали навески в специальных кюветах в термостате при повышенной температуре. О стабильности судили по количеству поглощаемого кислорода, во времени и по нарастанию кислотных чисел смазок. Установлено, что введение разработанных присадок в состав смазок приводит к уменьшению воды, вследствие гидрофильности композиции, что также снижает коррозию металлических частей механизмов.

**Ключевые слова:** присадка, антикоррозионная защита, синтез, механизм, депрессор, сыре, ресурс, реология, кинетика, скорость, вязкость.

## **Introduction**

Rational use of petroleum fuels and lubricants (POL), improving quality and expanding their range are one of the main tasks of the modern oil refining and petrochemical industry.

To achieve the intended goals, improving the physical and chemical properties of fuels and lubricants becomes very important and relevant. It is known that a large proportion of oils produced in our republic are paraffinic, i.e. containing a significant amount of alkanes of normal structure. The latter differ from other representatives of hydrocarbons in their increased pour point, which leads to a deterioration not only in the physicochemical properties of both the oils themselves and their processed products[1-4].

Various methods have been developed for the removal of paraffin hydrocarbons, in particular, urea dewaxing of diesel fuels and oils. But they are expensive, and the removal of paraffin hydrocarbons does not always have a beneficial effect on other properties of fuels and oils. Often, to ensure the required thermophysical properties of petroleum products, they resort to diluting them with lighter petroleum fractions. But this path contradicts the strategy of rational use of oil resources.

The most effective and cost-effective way to improve the physical-mechanical, chemical and thermophysical properties of oils, fuels and oils is the use of various additives. Unlike other methods, this direction ensures the rational use of oil resources and a comprehensive improvement in the physical,



mechanical, and applied properties of various petroleum products and oil in general. It is very important and relevant for the Republic of Uzbekistan to improve the physical and chemical properties of fuels and lubricants. This problem is aggravated by the fact that a large share of oils produced in our republic are paraffinic oils, i.e. containing a significant amount of alkanes of normal or slightly branched structure. The latter differ from other petroleum hydrocarbons by their increased pour point, which causes deteriorated temperature properties (mobility, fluidity, etc.) of both the oil itself and its processed products[5-8].

The urgency of the problem lies in the use of waste oil and fat and chemical industries - to obtain effective multifunctional additives for oils and lubricants of domestic products, recycling industrial waste, replacing expensive imported raw materials with local raw materials and thereby creating a systematic reduction in production costs, which is a necessary condition for profit growth and profitability of enterprises.

## **EXPERIMENTAL PART**

Freshly distilled solvents, previously freed from impurities, were used in the experiments. Their purity was controlled by readings of refraction, density and boiling point [9-10]. Isolation and purification of polymers and copolymers was carried out by reprecipitating them into a multiple excess of precipitant with intense stirring, followed by decantation from the solvent and drying to constant weight at room temperature.

The characteristic viscosity of polymer solutions was determined using a Ubellode viscometer, which provides multiple dilutions of the original solutions. The density of polymers was determined by pycnometry according to the method described in [11].

The thermal destruction of polymers was studied by differential thermogravimetric analysis on a Paulik-Paulik-Erdey derivatograph, based on measuring thermal effects when heating high-molecular compounds [12], (in the temperature range 293-773 K at a temperature rise rate of 1°/min.

Electron paramagnetic resonance (EPR) spectra were recorded on an E-4 model radio spectrometer (Varian company). The minimum concentration of spins that was available for recording by this device was  $10^{17}$ . The correct line shape and high resolution of the device were achieved at  $N_{mod} > 0.2 DN_{pp}$ , where  $N_{mod}$  is the modulation amplitude,  $DN_{pp}$  is the width of the first derivative of the EPR signal [13].

UV spectra were recorded on an SF-26 spectrophotometer and on spectrophotometer "SPECORD" in quartz cuvettes. Measurements of D were carried out from a series of solutions with different concentrations of monomers and in other experiments with a constant content of the initiator in them, at different temperatures.

IR absorption spectra of the samples were recorded on a UR-20 spectrophotometer from KARL-ZEISS using the method of pressing powders with KBr for polymers and copolymers and in a thin layer between glasses with KBr or KS1 for reagents in the liquid state [14]. NMR spectra of the samples were studied in deuterated dimethylformamide and methanol on a Bruker IC-200 spectrometer with an operating frequency of 200 MHz, at a temperature of 293 K. Chemical shifts of H are given relative to tetramethylsilane [15].



The chromatography of the released polymers was studied on a gas chromatograph from Atlas. The mobile phase in the chromatograph is an inert gas (nitrogen, helium). The sample is supplied in the form of vapor; the stationary phase is a solid. Diatomaceous earth was used as a carrier. The carrier is placed in spiral columns with a diameter 2 mm and 2 m long. A stationary phase is applied to the diatomite, which is selected empirically for each separation. The sample is introduced using a tap. The sample volume is small: 0.01 – 50  $\mu$ l. Then the inert carrier gas is purged [16].

## RESULTS OBTAINED AND THEIR DISCUSSION

The purpose of this work is to develop a technology for producing phosphorus-containing additives by phosphorylating waste from the oil and fat industry - gossypol resin using the Friedel-Crafts reaction.

A huge amount of research has been devoted to the development of modified derivatives of gossypol resin. However, these studies mainly relate to the production of additives such as antioxidants, antioxidants, and modifiers of the properties of polymer materials. There are still only a few reports in the literature on the synthesis of phosphorus-containing derivatives of gossypol resin, and the properties of these compounds and the possibility of obtaining additives for lubricating oils based on them have not been studied at all [17-18].

The gossypol molecule contains a large number of polar groups, in particular hydroxyl groups, however, due to the presence of two heavy dialkyl naphthalene nuclei, it is not soluble in water.

Of the six hydroxyl groups, the strongest intramolecular hydrogen bonds are formed by OH groups located in the ortho position to the aldehyde group. The shift of electrons towards the OH group simultaneously suppresses the acidic functions of this group and increases the electron-withdrawing ability of the aldehyde group [19].

Therefore, the hydroxylated group in gossypol should exhibit high activity in reactions with compounds whose molecules have atoms with lone electron pairs. For experimental studies, 5 samples of gossypol resin were taken, formed at various oil and fat processing plants in our republic, the structure of which was identified by IR and PMR spectroscopy.

Gossypol resin consists of 10-12% nitrogen-containing compounds, 65-70% products of oxidation and transformation of gossypol and 15-20% products of transformation of fatty acids in the form of lactones, as well as polymerization resins. The presence of phenolic products in the composition of gossypol resin allows it to be used as a novolac for polymer-analogous transformations, in this case for phosphorylation, as well as for the production of additives and modifiers of the properties of industrial lubricants based on them.

We modified gossypol resin using mild and effective phosphorylation methods [20]. The first stage of the work was the study of the phosphorylation of gossypol resin, and the best results were obtained using the methods of transesterification of phosphites and phenolysis of phosphamides.

Under the conditions found, almost all hydroxyl groups of the phenolic component react, as follows from the determination of the phosphorus content in the resulting product.

$AlCl_3$  and three times the calculated amount of  $PCl_3$  were added dropwise to the samples immersed in a container with glacial acetic acid. The temperature of the reaction mixture rose to 40°C and was maintained at this level during the reaction (Fig. 1). With increasing reaction time,



the phosphorus content in samples 1 and 2 increased, and the introduction of phosphoric acid groups into sample 2 at the initial stage is more effective (Fig. 2, 3).

Hydrolysis of the intermediate was accomplished by adding a minimal amount of water to the reaction mixture. In the case of sample 2, the product dissolved in the reaction mixture with the formation of a viscous brown mass. This circumstance led to certain difficulties associated with isolating the modified product. The isolated phosphorus-containing products of gossypol and gossypol resin are solid, insoluble, difficult-to-grind brown substances.

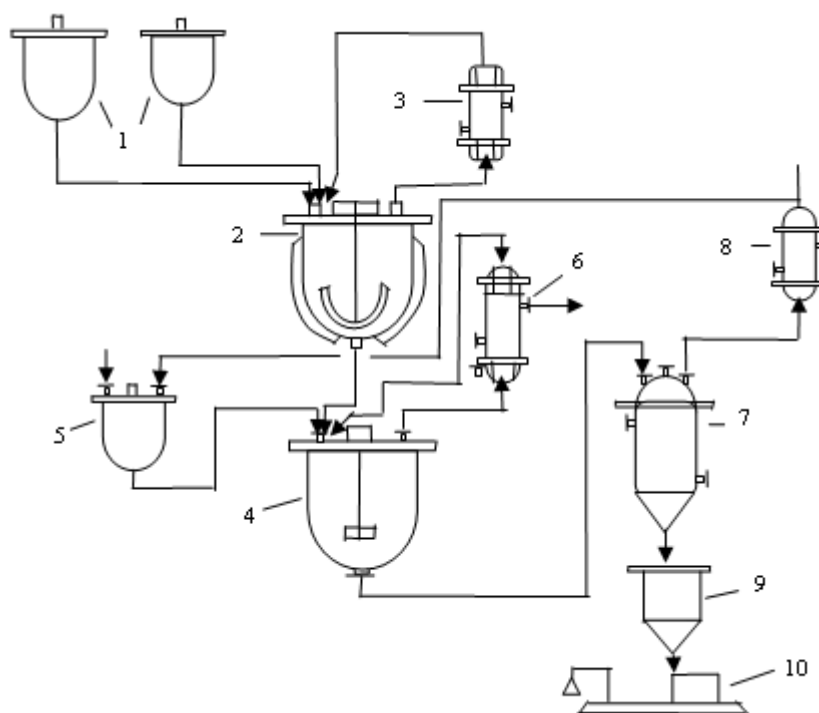


Fig. 1. Technological diagram of the phosphorylation process of gossypol resin. Bunkers – measuring tanks; 2-Reactor; 3,6,8-refrigerators; 4-Precipitator reactor; 5-precipitator container; 7-Drying; 9-Collection; 10-Libra.

They are highly soluble in water, ethanol and other polar organic solvents. In the IR spectrum of phosphorylated derivatives of gossypol and gossypol resin, new signals are observed in the region of  $2400\text{ cm}^{-1}$ , characteristic of P-H groups; wide and intense absorption bands appear in the regions of  $2650$  and  $2350\text{ cm}^{-1}$ , related to H-PO fragments. The absorption band of the  $\text{CH}_2=\text{CH}-$  group remains in the region of  $642\text{ cm}^{-1}$ . The presence of P-OH groups has also been proven by UV spectroscopy. The composition and structure of phosphorylated derivatives of gossypol and gossypol resin were confirmed, in addition to PMR and IR spectroscopy, also by the results of elemental analysis and gel permeation chromatography (Table 1).

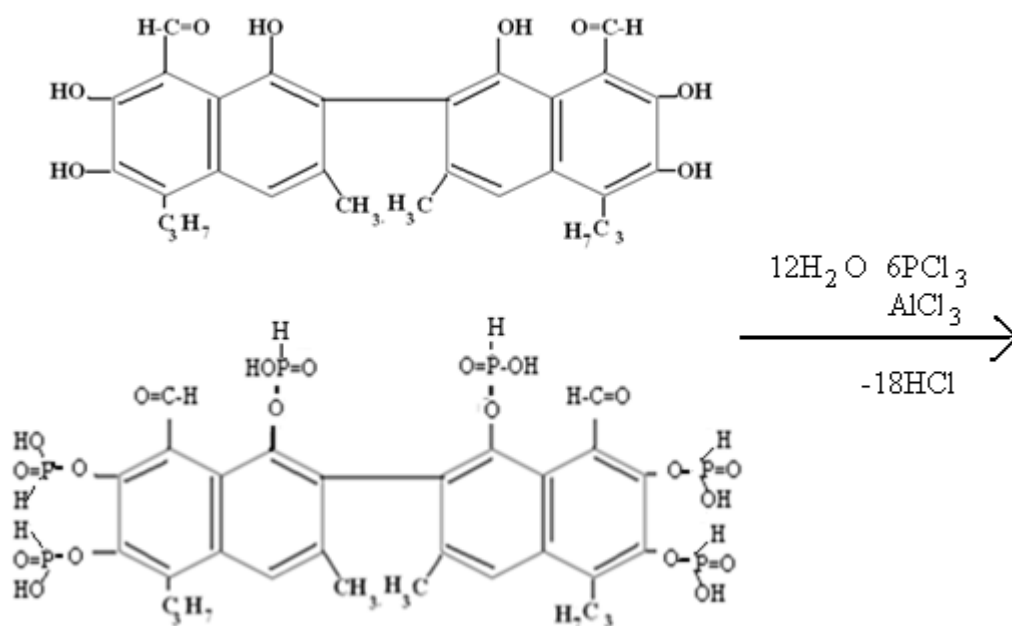
Table 1. Properties of additives obtained by phosphorylation of gossypol and gossypol resin with phosphorus trichloride.



Sample	Duration of reaction hours.	Degree transform- nia, %	Acidic number of 0.1 N NaOH, mg/equiv/g	Content, %			
				phosphorus		-C=C-	N -C=O
				Find- But	Calculated by number		
1	3	48	2.4	7.63	7.50	9	26.5
	5	65	3.4	10.42	10.64	2	18.1
	10	77	3.7	12.35	11.47	No	17.1
2	3	63	3.1	10.13	9.61	2.6	24.1
	5	67.6	3.4	10.82	10.53	2.5	23.0
	10	75	3.8	12.00	11.78	2.2	22.7

Based on the data obtained, it can be assumed that here the cross-linking of oligomeric chains occurs at C-OH groups with the formation of P-O-P bonds.

Based on spectral and physicochemical methods of analysis, the reaction scheme for the phosphorylation of gossypol resin can be represented as follows:



The results of laboratory studies, as well as pilot and industrial tests showed the promise of practical application of the synthesized additives, for the production of which the product was developed

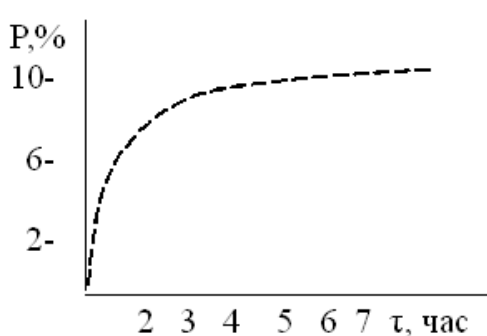
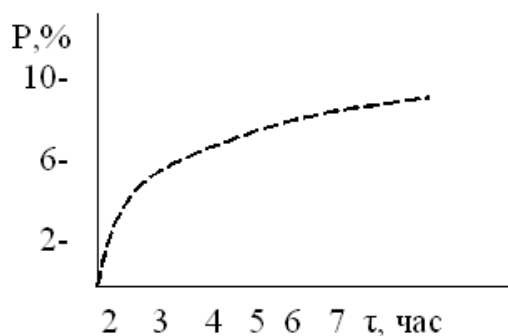


Fig.2. Dependence of changes in phospho content in the phospholation product.

Fig.3. Dependence of changes in the content phosphoric acid groups in the phospholati product

technology for producing phosphorus-containing additives based on gossypol resin and PC13, Friedel-Crafts catalysts and various phosphorylating agents.

A study of the influence of the molecular weight distribution of the additive synthesized based on the phosphorylation reaction of gossypol resin on their properties as an oil depressant led to the following results. In the gel chromatograms of the developed additive (Fig. 3), in some cases, in addition to the peak of the main substance, a peak of a low molecular weight fraction-impurity ( $M = 500$ ) and a peak of a high molecular weight fraction ( $M = 1500-20000$ ) were detected. The presence of the latter greatly affects the value of Mw, with virtually no effect on Mn, which ultimately leads to a significant change in the Mw/Mn ratio.

It was found that lubricants modified with the developed additives are not subject to syneresis, while it was found that fillers (for example, graphite) also increase the colloidal stability of lubricants.

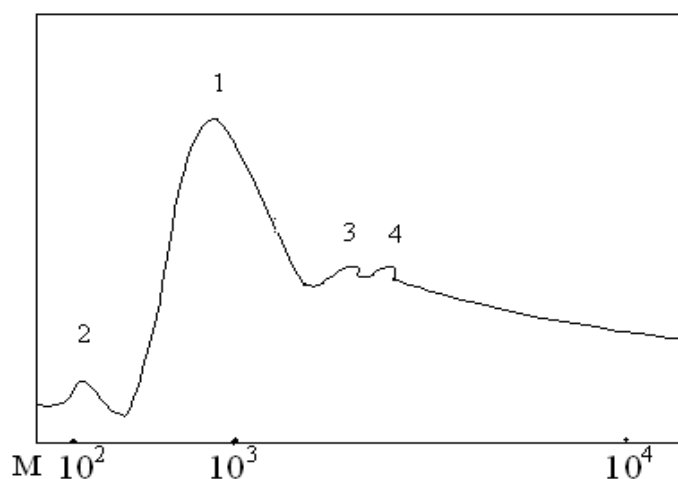


Fig.4. Gel chromatograms of the synthesized additive based on the phosphorylation reaction of gossypol resin: 1-main substance, 2-low molecular weight impurity, 3-high molecular weight fraction, 4-peak in the exclusion region.

The chemical stability of lubricants was determined by oxidizing a sample of them in a bomb under oxygen pressure (8 atm) at  $100^\circ\text{C}$  or by keeping the samples in special cuvettes in a thermostat at an elevated temperature. Stability was judged by the amount of oxygen absorbed over time and by the increase in acid numbers of the lubricants.

It has been established that the introduction of the developed additives into the composition of lubricants leads to a decrease in water due to the hydrophilicity of the composition, which also reduces the corrosion of metal parts of mechanisms.

Acidity and acid number lubricants modified with additives developed by us were determined according to GOST 5985 - 59. The indicator was nitrosine yellow (delta) or phenolphthalein. When testing many lubricants and specialty oils containing oxidized petroleum products, the acid numbers determined using nitrosine yellow and phenolphthalein did not coincide.



The viscosity of greases was measured using an automatic capillary viscometer, since it determines the possibility of their filling into the starting mechanisms of cars, as well as power loss due to friction. It is especially important to know the viscosity of lubricants at low temperatures. At constant temperature, viscosity changes depending on the rate of deformation of the lubricants. Typically, lubricant standards regulate the maximum permissible viscosity value at a particular low temperature and deformation rate.

Shear strength is the minimum shear stress that causes failure of the grease's structural framework and its transition to viscous flow. This indicator was measured on a K-2 capillary plastometer.

The effect of a depressant on the crystallographic lattice of n-alkanes was studied using IR spectroscopic studies of n-alkane crystals isolated from solutions in individual solvents and from diesel fuels in the presence of 0.1-5% of various depressants (Ferad, FSP-1, FSP -2).

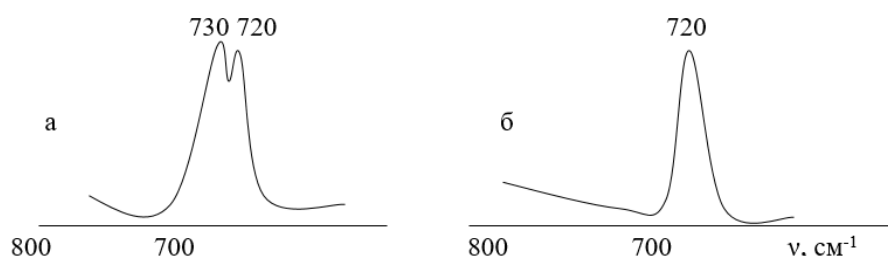


Fig. 5 IR spectra of a petroleum product with a melting point of 52.90 C in the region of 730-720 cm-2: a) in the presence of an additive (P-1) – hexagonal modification, b) in the absence of an additive – rhombic modification.

It was found that the size of the unit cells and the type of spatial lattices of n-alkane crystals do not change with the addition of depressants. This allows us to conclude that when exposed to a depressant, the formation of volumetrically mixed crystals between the molecules of n-alkanes and the depressant does not occur.

According to IR spectroscopic studies, under the influence of intermolecular interactions that arise between atoms in a unit cell, splitting of the absorption band in the spectrum of an oil product can occur. For example, the nature of the absorption band of pendulum vibrations (CH<sub>2</sub>)<sub>n</sub> in petroleum products with polymethylene chains is determined by the crystal lattice (Fig. 4). The shift of absorption bands under the influence of intermolecular interactions (with the exception of compounds with strong hydrogen bonds) rarely exceeds 25 cm<sup>-2</sup>. Only in the low-frequency region are significant changes in the spectra sometimes observed.

Product Introduction phosphorylation reactions of gossypol resin, which has depressant activity, leads to a decrease in the size of n-alkane crystals by approximately 10 times. In the presence of resinous compounds as a depressant, the crystals have a lower degree of symmetry, which are irregular plates. The presented experimental results indicate various modifications in the morphology of n-alkane crystals under the influence of the new depressant additives we have developed.

The studies carried out to identify the electrical properties of additives showed that three sections are marked on the curves of the dependence of dielectric constant on temperature. In the first of





them, as cooling occurs, the dielectric constant changes linearly up to the cloud point; in the second section, an anomalous dependence is observed up to the solidification temperature; in the third, the dielectric constant is practically independent of temperature. From an analysis of the melting curves (heating began immediately after the solutions solidified), it was concluded that this process occurs differently: the transition of the liquid phase to the solid phase and vice versa has a hysteretic character.

The study of electrical phenomena during the directional crystallization of petroleum product paraffins showed that they occur not by electronic, but by polarization mechanism. This suggests that the thermodielectric effect is based on the polarization of depressant molecules in the crystallization front and their accumulation in the solid phase, as a result of which the paraffin becomes a carrier of the electric field.

Polymer depressants have one or another molecular weight polydispersity, so it seems interesting to determine the effective molecular weight of that part of the depressant that directly interacts with paraffin crystals. For this purpose, solutions of polyol based on phosphorylation reactions of gossypol resin in hexane and in model fuel. The molecular weights of the crystalline part and the filtrate were measured using gel permeation chromatography. The molecular weight of the polyol from the precipitated part of mixtures involving n-alkane is lower than that of the polyol isolated in the absence of n-alkane. This is explained by the fact that polyol components with a relatively low molecular weight, which do not precipitate in the absence of n-alkane, coprecipitate with the latter if it is present in the system. It is believed that these components of the additive are responsible for its effectiveness in reducing the pour point. The interaction of n-alkane crystals and the copolymer is confirmed by the data of the IR spectra of the precipitated substance, in which a polyol is detected based on the strong carbonyl absorption band, which does not precipitate in the absence of n-alkane. With the introduction of additives of various compositions, a decrease in viscosity and duration of fuel filtration is observed. However, in the presence of the additive we developed at temperatures below  $-5^{\circ}\text{C}$ , an episodic restoration of viscosity and elasticity is simultaneously observed. This is most likely explained by the fact that when an additive based on phosphorus-containing compounds is added at the initial stage of cooling, very small crystals are formed, which are then grouped into large particles as their number increases during the cooling process.

Comparison of the solubility of polyols with their depressant activity in different fuels made it possible to formulate a criterion for the acceptability of fuel to the additive: the copolymer is most effective in the fuel whose pour point corresponds more closely than others to the solubility of the polyol, characterized by its cloud point. Thus, a polyol with a molecular weight of  $16 \cdot 10^3$  ( $t_n = 30^{\circ}\text{C}$ ) is most effective in fuel with a pour point of  $24^{\circ}\text{C}$ , a polyol with a molecular weight of  $8 \cdot 10^3$  ( $t = 12^{\circ}\text{C}$ ) is most effective in fuel with a pour point of  $9^{\circ}\text{C}$  etc.

## CONCLUSION

Based on the research results, technological regulations have been developed for the technology of using phosphorus-containing derivatives of gossypol resin as an additive to lubricants. The developed technologies underwent pilot testing at the Alti-Aryk oil refinery according to temporary technological regulations.



Thus, using the methods of chemical, physicochemical and elemental analysis, the main physicochemical and kinetic parameters of the process of phosphorylation of gossypol and gossypol resin, as well as some properties of the phosphorylated products of the latter, were determined.

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