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Synthesis and Properties of Depressators Based on Sopolymers in the Presence of Gossypol Pitch

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ABSTRACT

Nowadays search of ways of obtainment new, more effective depressants for base oils is especially actual. Action of pour-point depressants is reduced to their influence on processes of crystallisation and structurizations of firm, first of all, paraffin hydrocarbons. In the given work we investigated depressants influence on some physical and chemical properties of oil distillates of the Kumkol deposit on the basis of the oil waste and a waste of oil-fatty industries. Concentration of entered additives and efficiency of their action depend on temperature of input of an additive, structure and quantity of paraffinic hydrocarbons, the asphaltenes and pitches maintenance, and also their ratio.

Key words: Kumkol oil, depressants, oils, gossypol, pitch, polycondensation, Sulphating, congelation temperature, paraffinic hydrocarbons.

INTRODUCTION

At present in Kazakhstan there is no production of depressants for preparation of base oils for transportation and processing. In this connection the development and application of new highly effective reagents is actual.

In most cases the pour-point depressants in Kazakhstan are imported, basically the Russian and foreign manufacture. Delivered pour-point depressants by the chemical nature and physical-chemical properties are close, because basically they concern to vynilacetate and acrylate, or to the mixed type of additives[3].

Kumkol oil is comparatively easy (0,81-0,83 g/sm^3), with considerable content of easy fractions and practical absence of average impurity. The high content of paraffins in oil leads to waxing of the underground and terrestrial equipment of oil wells. The basic rheological and physical-chemical characteristics of Kumkol oil are presented in the table 1.

It is known that efficiency of pour-point depressants is defined by decrease in solidification temperature of oil products and concentration of the additives providing maximum depressor effect.

Pour-point depressants for oils, oil products and oils by the chemical nature are, as a rule, polymeric substances. Concentrations of depressor are selected in dependence with purpose and conditions of application of an additive. The optimum temperature of depressor input to oils of highly paraffinic crude lies in a range of 50-70^{0}C [1-6].

Obtaining of pour-point depressants and their use as depressators in oil products, especially in base oils of Kumkol crude are rather actual at industrially-innovative development of the Kazakhstan economy as a whole.

The defining factor of technical perfection of the engine is functional properties of engine oil. Modern lubricants are capable to maintain for a long time high mechanical and thermal load, to protect from deterioration, corrosion and formation of the deposits breaking normal work of the aggregate and to provide decrease in losses of energy.

Quality of lubricant oil can be improved in two ways:

a) Improvement of properties of base oil at its reception;
b) Alloying of oils by additives[2-4].

Additives – synthetical chemical compounds, entered into base oil for improvement of their properties in the periods of exploitation and storage. Practically all trade vehicular oils are produced with additives, their number reach up 8 various compounds, and general mass content – up to 25%.

Almost all additives, both single, and packages, are delivered on oilmixer factories in the form of solutions of additives in the oil, containing about 50% of active substance. In receipts are underlined not content of a pure additive, but quantity of a trade product of an additive, i.e. its solution. Therefore the instructions about presence in oil of 25 % of additives yet do not specify real quantity of active substances. At the analysis of ready or working oils, the expenditure of additives is defined and the maintenance of active elements of additives is calculated. Some additives influence on physical properties of base oils, others render chemical effect. They can supplement each other that creates synergetic effect, but can cause and antagonistic effect. Many modern additives carry out some functions. On the market more often deliver compositions of additives - packages (additivepackage). These are the packages of strictly certain structure intended for oil of concrete appointment and a class of quality.

Packages of additives are delivered in the form of the concentrated solution of additives in oil (to 50 % of active substances). Such composition is entered into base oil and after mixing the trade oil is obtained ready to usage.

In many cases the oils even received with application of the advanced methods of purifying, not completely satisfy to requirements of consumers. To provide necessary exploitation properties is possible by means of addition to base oil - the cleared oil fraction - various additives.

In same time, the high requirements to operational properties of modern oils, cannot be provided only by choice of raw materials and technology of its purification. For improvement of properties of oils (and sometimes giving new, which oils do not possess) at a finishing stage of preparation (at compounding) into them enter the additives. Additives not only improve exploitation properties of oils, but also essentially reduce the expense of the latter. As additives to oils some thousand organic compounds are studied and offered. However industrial production and practical usage have received not more than 100 products and compositions.

Synthesis and industrial production of additives the world production of which exceeds 1,5 million t/year, is important independent branch of oil chemistry. In the greatest quantity produce sulphonates of metalls, derivatives of alkylphenols and ditiophosphoric acids, products of oxidation of paraffinic hydrocarbons and their salts. Industrial production of the first in the CIS of additive to oils AzNII - CIATIM-1 (depressor, decreasing the solidification temperature of oils) has begun in the

end of 40-years.

Efficiency of additives depends on depth of purification of oils, their nature and structure. Additives depending on type and concentration improve one or several indicators of exploitation properties of oils, but can worsen thus others indicators. Therefore it is necessary to reveal collateral negative action of additives and to search for ways of elimination or easing of this action. Use of additives compositions of different function in oils is perspective. Thus it is important to establish an optimum quantitative parity of separate components.

Additives to oils are classified by destination (functional action), chemical composition and action mechanism. The most developed and extended is the first classification according to which allocate next groups of the additives improving those or other properties of oils: raising stability of oils to oxidation - antioxidative (sometimes they are called inhibitors of oxidation); increasing lubricant ability of oils - antifrictional, antiweared and antiwelding; promoting protection of metals against corrosion - inhibitors of corrosion and anticorrosive; not supposing the formations on details of the engine of scales, varnishes and deposits - washing, or detergent-dispersive; lowering the solidification temperature - depressors; improving viscosity-temperature properties - viscosity; raising stability of oils to influence of fungi and bacteria – inhibitors of microbiological defeat, or antiseptics; preventive foaming and emulsification of oils - antifoam and deemulsifying; raising adhesion and preventing oils spreading - adhesive; improving simultaneously a few exploitation properties of oils - multifunctional.

Classification of additives on destination is not absolutely strict, because the products referring to certain group, to a greater or lesser degree influence on other properties of oils. So, depressors influence on viscosity-temperature properties of oils at low temperature, inhibitors of corrosion can brake oxidation, and antiwearing additives - to strengthen or reduce corrosion of metals. In this connection the search of multifunctional additives improving simultaneously few of exploitational properties of oils is conducted, or are developed the compositions of additives, similarly operating and consisting of 3-7 products of different structure.

Chemical classification of additives provides their division on composition of active (polar) group and structure of hydrocarbonic (non polar) group. By composition of active group allocate the oxygen-, sulphurus-, phosphorus - nitrogen - chlorine - and boroncontaining additives. Also are used organic compounds, containing two-three active groups in a molecule, - sulphur-nitrogen - sulphurhlorine – phosphorus oxygen containing. Additives can be subdivided also on metalcontaining (ashy) and not containing metals (ashless). The most part of additives are referred to the first group. The major characteristics of additives, belonging to the class of surfactants, are their polarity and polarizability, conditioned by various functional groups, defining dipole moment and other electrophysical properties. For compounds of the same class the polarity decreases with growth of length of a hydrocarbonic radical (or a hydrocarbonic part of molecule) and molecular weight of compound at identical structure and number of active groups. Polarity and polarizability of molecules (mycelles) of additives substantially defines their functional efficiency.

Classification of additives on the mechanism of action reveals the reasons determinant display of their efficiency. On the basis of action of the majority of additives lie superficial phenomenons (i.e. the processes proceeding on an interface and connected with superficial energy) that allows conditionally subdivide additives on adsorption-active and adsorption - inactive.

The mechanism of action of adsorption-active additives is based on change of a energetic condition of interfaces «a firm body - oil», occurring already in the presence of small quantities of additives (detergents, depressors, antifrictional: etc.). Such change can occur to surfaces of metal and firm particles, dispersed in oil, carbonaceous substances and firm hydrocarbons. Distinctions in properties and condition of a firm surface and following from here the different requirements to structure of additives allow allocating products of the bulk and superficial action. The first regulate

interaction of firm particles directly in oil volume: depressor additives - particles of firm hydrocarbons, detergent-dispersive additives - particles of carbonaceous substances; the second - on border of section of phases "metal-oil" or directly the superficial properties of the metal that leads to adsorption lowering of its durability (plastiñizing of metal). Action of adsorption-active additives is connected with low polarity of oil products that causes high sensibility of additives to extraneous surfactants and first of all to the water, as a rule, present at small quantities in oils. Efficiency of adsorption-inactive additives is revealed in their chemical or physical interaction with hydrocarbonic or other components of oil. As an example of additives of the physical mechanism of action can serve viscous polymeric additives, role of which boils down to improvement of viscous - temperature properties of oils.

Additives add to all types of engine oils, to turbine, compressor, transformer, transmission and to some industrial oils.

It is known tha[2,4] at definition of optimum characteristics of depressor it is important to choose its minimum concentration providing maximum depressor effect, because in volume of oils constantly proceed processes of structuralization that additive might provide necessary solidification temperature of oils.

MATERIAL AND METHODS

Researches of oil distillates of Kumkol oil (table 2) have shown that these fractions are slightly resinous and contain significant amounts of 72,5 % and 78,3 % of parafin-neften hydrocarbons. Physical-chemical properties and group chemical compound of the investigated samples of oil distillates are in close interrelation with their fractional structure.

So, the second oil distillate (fraction of 420-480^{0}Ñ) in comparison with the third oil distillate (fraction 480-500^{0}Ñ) has smaller values of density, kinematic viscosity, factor of refraction, temperature of solidification and average molecular weight.

Higher values of such indicators as refraction factor, the viscous-weight constant, an aniline point and a specific dispersion, for the third oil distillate specify the higher degree of aromatizing that confirmed by researches of group chemical compositions of both products.

At the same time the analysis of carbon distribution in investigated samples shows that quantity of the carbon which is a part of aromatic structures of both products is identical. However, the most quantity of the carbon which is a part naphthenic structure of the third oil distillate specifies in presence in it a big quantity of naphthenic hydrocarbons with high factor of refraction of a group chemical compound. In this respect usage of depressants is considered as the perspective and economic.

It is known that efficiency of pour-point depressants is defined by decrease in temperature of solidification of oils, reached in their presence, and concentration of the additives providing maximum depressor effect.

Pour-point depressants to oils by the chemical nature are, as a rule, polymeric substances. Concentration of depressors is selected in dependence with purpose and conditions of application of an additive. The optimum temperature of input depressor in highly paraffinic oils lies in a range of 50-70^{0}Ñ[1-6].

Base oils of Kumkol oil are referred to highly paraffinic oils. In this connection the delivered pour-point depressants do not satisfy growing requirements because of low efficiency and various conditions of application.

One of effective depressants is depressators of natural origin i.e. liquid resinous components of oils.

In this connection the ways of obtainment of depressants on the basis of copolymers vinylacetate, styrene and further polycondensation of aminophenol and a waste of oil-fatty industry are developed for improvement of operational properties of oil and base oils of the Kumkol deposit. The wastes of oil-fatty industry gossypol pitch are cubic wastes of vacuum distillation of the fatty acids,

received from cotton soap stocks at processing of seeds and cotton oils. It is a homogeneous plastic mass from dark brown to black colour.

Typical structure of gossypol pitch (Shymkent oil-fat combinat): 98,29 % of organic substances; 1,71 % of inorganic substances; 100 % of ether-soluble substances; acid number 68,5 mg of KOH/g; iodic number 97g; saponification number 200 mg of KOH/g; radio number 135 mg of KOH/g; hydroxyl number of 91%; fatty acids released at saponification from 52 to 64%; crude fat acids and their derivatives, other part - products of condensation and polymerisation gossypol and its transformations formed at extraction of oil, mainly, in the course of distillation of fatty acids from soap stocks, 38 % of low-fat substances; 0,2165 % of phosphorus (in recalculation on P2O5); 8,78 % of calcium in calcium salts. Properties of gossypol pitch depend on quality of initial raw material, observance of technological modes of decomposition of fats, depth of distillation of the received fatty acids and other factors. In gossypol pitch are uncovered 12% of nitrogen-containing compounds, 36% of products of gossypol conversion and 64% of fatty and oxyfatty acids. Content of fatty acids in pitch makes up 64%. Along with free, also associated fatty acids are present in composition of di—and triglycerides.

Depressator DPN-4 is produced on the basis of vinyl acetate and sterol by method of sopolymerization in the presence of benzoyl peroxide at temperature of 60-110^{0}C during 4-6 hours. Then to mixture add fraction of polycondensation of aminophenol and oil-fatty industry wastes – gossypol pitch – without and in presence of formalin in alkaline medium at temperature of 80-90^{0}C during 2-2,5 hours. For extraction of unsaponifiable fractions through vacuum evaporator enter white spirit with further separation of fractions. Received semi-product consists of 60-70% from sodium salts, predominately unsaturated fatty acids with prevalent fraction of C_{11}-C_{17}. In this product adds sodium sulphate Na_2SO_3 up to obtaining homogeneous mass.

Dependence of change Kumkol oil solidification temperature from concentration of pour-point depressants are given in the table 3.

Studies show lowering of oil solidification temperature from 12 to -2^{0}C with use of depressants. Oil solidification temperature without depressant is equal 12^{0}C.

Researches of influence of synthesized additives DPN-4 concentration (0,1-0,005%) on solidification temperature showed that at addition of them from (0,1-0,005%) the Kumkol oil olidification temperature is decreased.

But concentration of entered additives and efficiency of their action depend on temperature of additives input, on composition and quantity of paraffinic hydrocarbons, content of asphaltenes, as well as their ratio.

As was noted above, input of DPN-4 additive allows to decrease oil solidification temperature and thereby to improve its fluidity and appropriately to decrease pressure in pipeline and to improve oil outlet efficiency from cisterns.

Thus, it is revealed that, efficiency of action of additives of DPN-4 series depends on the content of asphaltenes, pitches, paraffins in oil.

Also we investigated influence of synthesized additives DPN-4 on physical-chemical properties on base oils of Kumkol oil. It is known that complexity of all available light fractions in volume of 78% from investigated oils slightly influence on decrease of oils solidification temperature. For decrease of oils solidification temperature are used synthesized depressants DPN-4 on the basis of sopolymers in the presence of gossypol pitch.

Dependence of change of oils solidification temperature of Kumkol oil from concentration of pour-point depressants are presented in the table 4.

Researches at usage of depressants show decreasing of oils solidification temperature of fraction 420–480^{0}C from 27,5 to – 7^{0}C, and for fraction 480–500^{0}C from 35,0 to – 4 ^{0}C.

Base oils solidification temperature of fraction 420–480^{0}C without depressants is equal 1^{0}C, for fraction 480–500^{0}C - 30^{0}C.

RESULT AND DISCUSSION

Study of influence of concentrations (0,1-0,005%) of synthesized additives DPM-4 on base oils solidification temperature of Kumkol crude showed that at their addition from (0,1-0,005%) the base oils solidification temperature of Kumkol crude is decreased.

Nevertheless, concentration of entered

Table 1: Basic rheological and physical-chemical characteristics of Kumkol oil

Indicator 1	Value 2	SST and methods 3
Density at 20° C, kg/m^3	811,7	3900-82
Molecular mass	230	
Kinematic viscosity at 50°C, mm^2/c	3,53	33-82
Congelation temperature, °C	12	20287-74
Acid number, mg KOH/1	0,04	5985-79
Coking ability % mass	1,61	1933-74
Content: % mass		
Asphaltenes	0,3	
Silica gel gums	6,5	
Paraffin melting point °C	13,9/51	11851-85
Sulphur general	0,1	Method of HII

Table 2: Basic rheological and physical-chemical characteristics of base oils of Kumkol oil

N° n/n	Name of indicators	2–nd oil distillate fraction 420–480°C	3–rd oil distillate fraction 480–500°C
1	Density ρ^{20}_4	0,8851	0,9016
2	Refraction coefficient n^D_{50}	1,4780	1,4850
3	Viscosity, υ50	14,9	36,7
	υ_{100}	4,1	7,4
4	Viscosity–gravity constant	0,837	0,849
5	Intercept of refraction	1,0475	1,0462
6	Temperature of solidification, ^{0}C	27,5	35,0
7	Average molecular weight	340	410
8	Specific dispersion	140	151
9	Aniline point, ^{0}C	90	97
10	Group chemical composition, %		
	Paraffin-naphthenic hydrocarbons	78,3	72,3
	Light aromatic hydrocarbons	8,8	9,9
	Average aromatic hydrocarbons	5,5	6,2
	Heavy aromatic hydrocarbons	6,0	8,5
	gums	1,4	2,9
	Group structure composition, % C_P	59	53,5
	C_N	30	35,5
	$C_À$	11	11
11	Index of viscosity	–	83
12	Flash temperature, ^{0}C	–	206

additives and efficiency of their action depend on temperature of additive input, from composition and quantity of paraffinic hydrocarbons, content of asphaltenes and gums, as well as their ratio.

As was mentionad above, input of additive DPM-3 allows to decrease of oils solidification temperature and thereby to improve their fluidity, accordingly to facilitate and to reduce in price their further processing, namely dewaxing.

Thereby, it is revealed that efficiency of action of additives of series DPN-4 depend on content of asphaltenes, gums, paraffins in oils.

Table 3: Experimental data on usage of additive DPN -4 by SST 20287-74

Oil	Volume, ml	Volume of additive, %	$T_{solidification}$ °C with additive DPN-4
Kumkol oil	100	-	12
	100	0,005	10
	100	0,001	8
	100	0,05	6
	100	0,025	3
	100	0,01	1
	100	0,1	-2

Table 4: Experimental data on use of additive DPN-4 on SST 20287-74

Oil	Volume, ml	Volume of additive, %	$T_{solid.}$ °C with additive DPN-4 2–nd oil distillate of fraction 420–480°C	$T_{solid.}$ °C with additive DPN -4 3–rd oil distillate of fraction 480–500°C
Base oils of Kumkol crude	100	-	27,5	35,0
	100	0,005	19,5	28,9
	100	0,001	14,0	22,7
	100	0,05	9,8	15,0
	100	0,025	4,8	11,5
	100	0,01	1,5	5,0
	100	0,1	-9	-6

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