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Improving the Quality of Base and Commercial Oils

A. F. Khuzhakulov
Bukhara Institute of Engineering and Technology, Bukhara

Annotation: This article summarizes the results of research over the past 15-20 years in the field of improving the production efficiency of lubricating oils with maximum use of available capacities and optimizing the quality of finished products according to modern technological requirements.

Key words: oil, purification, phenol, petroleum oils, raffinate, residual oils, hydrocarbon composition, viscosity, viscosity index, extract, dispersed system.

Works in the field of chemistry and technology of lubricants are one of the main research areas of the scientific school of Professor B.N. Khamidov, established more than 40 years ago. The results of the research of this school have significantly expanded the understanding of the peculiarities of the production and use of oils and lubricants, the influence of the nature of raw materials on the relationship between the composition (colloidal structure) and the properties of the resulting commodity products. As a result, a number of important provisions were formed for the improvement and intensification of processes, fundamentally new technological solutions were proposed for the processes of selective purification, dewaxing and deoiling with the help of external influences - force fields, small amounts of surfactants (technological additives) and their joint application.

Started in the 80s, these works were successfully continued under the leadership of Doctor of Technical Sciences B.N. Khamidov in close cooperation with producers of petroleum oils in a number of the largest refineries of the country. This article summarizes the results of research over the past 15-20 years in the field of improving the production efficiency of lubricating oils with maximum use of available capacities and optimizing the quality of finished products according to modern technological requirements. Recall that the required level of quality of the commercial product is achieved by using the base oil of optimal chemical composition and a balanced composition of additives of the necessary functional action. The chemical composition of the base depends on the nature of the raw materials and the technological parameters of its processing processes, taking into account their possible modernization without reducing the selection of the target product.

The process of selective cleaning. One of the ways of its intensification involves increasing the selective ability of the solvent and the possibility of regulating the conditions of phase redistribution. Thus, the use of N-methylpyrrolidone (N-MP) instead of furfural, which has a higher solvent capacity due to the shielding of the atom in the molecule by a methyl group and the strengthening of dispersion forces, allows for the corresponding modes of countercurrent three-stage purification of distillate 330-420 and 420-490 ^{0}C to increase the yield of refined products by 1.8 and 5.5% (wt), respectively, to reduce the consumption of N-MP compared with furfural by 1.6 and 1.4 times and reduce the temperature in the extraction columns. The obtained raffinates are characterized by a higher viscosity index and a reduced sulfur content (Table. 1) (3).

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Table 1

Indicators	Selective purification raffinates			
	330 – 420 ^{0}C		420 – 490 ^{0}C	
	N-MP*	phenol**	N-MP*	phenol**
Solvent:raw material (mass)	1,2:1/1,3:1	2:1	1,5:1/1,8:1	2,2:1
Temperature in the extractor, ^{0}C above below	 50/60 35/43	 97 71	 64/72 44/51	 112 100
Yield, % (mass)	60,4/46,6	58,6	54,4/46,1	60
Density at 50 ^{0}C, kg/m3	846,9/0	846,8	859,5/0	862,3
Viscosity, mm2/s at 50 ^{0}C at 100 ^{0}C	 15,3/16,2 4,5/4,6	 15,6 4,5	 33,4/34,1 7,7/7,7	 34,8 7,9
Refractive index at 50 ^{0}C	1,4700/1,4686	1,4700	1,4755/1,4775	1,4775
Melting point, ^{0}C	27/-	27	39,4/-	38,8
Viscosity index	132/177-122	126	117/111-113	115
Content, % (wt.) of Sulfur in raffinate Water in the solvent	 0,62/- 0/0,4-1	 0,7 -	 0,7/- 0/0,4-1	 0,81 -
*	In the numerator – laboratory data, in the denominator - factory data			
**	Distillate purification in laboratory conditions according to the plant regime			

Additional increase in the selection of the same refined products by 2.8 and 3.2% (wt.) accordingly, the use of technological additives contributes (0.0005-0.002% by weight. on raw materials), stabilized with calcium carbonate dispersion soaps. Due to their surface activity, these additives regulate the properties of the system at the interface, solubilize heavy aromatic hydrocarbons and raw materials resins. By increasing the selectivity of the solvent, the additives are concentrated in the extract solution and only 14-16% (wt.) from their total number passes into raffinates. An indispensable condition for the effective purification of distillates should be to prevent its "greasing" as a result of the capture of droplets of raffinate and extract by solvent and water vapors, as well as decomposition products during solvent regeneration. The vapor-liquid mixture formed in the steam columns during cooling gives an emulsion of a direct type, where the so-called light oil serves as the dispersed phase. The resins contained therein form an adsorption layer on the surface of the oil droplets, which increases the structural and mechanical properties of the surface layer and the stability of the emulsion. In order to destabilize the most stable emulsion of the composition of 43.4% "light" oil - 42.6% N-MP – 14% water, nonionic surfactants – copolymers of oxypropylene and ethylene of domestic and foreign production were studied. Data on their effectiveness – the amount of oil released in 90 minutes (% vol.) are given below:

No PAHs 21,9

With 12.5 g PAH 1 t.

D-157...81,2

Reopon-4C...21,9

Naphthenol– 1..21,9

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Naphthenol– 3..35,6

Naphthenol– 5..21,9

Naphthenol– 7..21,9

APOSTILLE) 21,9

R-11 (Japan) 82,9

Further research has shown that with increasing concentration, the effectiveness of the most effective demulsifiers increases 2-3 times. This gave reason to recommend reagents D – 157 and Neftenol – 3 as destroyers of such emulsions for the technology of purification of N-MP oil raw materials developed and implemented at the FNPZ plant. The dewaxing process following in the oil production scheme is proposed to be intensified also with the help of technological surfactants – modifying additives. Such additives make it possible, without additional investment, to increase the selection of dewaxed oils from their potential content in raw materials, while simultaneously improving the quality of this target, as well as by-products. Adsorbed on growing crystals of solid hydrocarbons. Surfactants regulate the size and degree of their aggregation, change the amount of the liquid phase entering the solvate shells when cooling the raw material solution in the crystallizers. It is obvious that the surfactants available in the product fleet of this refinery are the most preferred as modifying additives. In Ferghana, oil–soluble surfactants PMA "D" and Detersol – 50 were studied as such for the dewaxing of residual raffinate under conditions as close as possible to factory conditions.

The most effective was Detersol – 50, acting as a metal-containing surfactant by the adsorption mechanism (8). Thanks to its use, the filtration rate of the raw suspension increased by 1.5 times, the yield of dewaxed oil – by 4.7%; the oil content in petrolatum decreased from 24.2 to 15% (wt.). At the same time, the optimal concentration Detersol – 50 (0.0005% by weight. on raw materials) turned out to be 1000 times lower than the concentration of the SDA – 1615 dewaxing additive recommended by Shell. In addition, when using the latter, additional safety measures must be taken in toluene or ketone - aromatic solvent. Pilot tests of Detersol – 50 as a dewaxing additive in the FNPZ showed that at a concentration of 0.0001-0.0010% (wt.) for raw materials, it allows, without deterioration of quality, to increase the selection of residual dewaxed oil by an average of 5% (wt.), the productivity of the plant for raw materials – by 17%. The introduction of this technology in 2008 improved the technical and economic indicators of the process of dewaxing residual raffinate.

Composition and properties of raw oil mixtures. One of the main conditions for the intensification of oil production is a constant composition of raw materials. Without observing the modes of technological processes, neither the use of effective solvents will allow to obtain oils of the required quality. Oil obtained from raw materials of the worst composition contains fewer high-index components and more resins (4.5).

The analysis of the components of base oils obtained from low-viscosity, medium-viscous and residual oils during phenol purification at the Ferghana Refinery recorded a significant difference in their properties, including compliance with the criteria of international standards. In terms of viscosity-temperature properties, only low-viscosity oils produced in the FNPZ meet the international requirement: IV = 97-121 (Table 2).

Table 2

Indicators	Components of base oils produced by FNPZ		
	low viscosity	medium viscous	residual
Viscosity, mm2/s at 50 ^{0}C at 100 ^{0}C	18,8 4,95	52,1 11	135,8 19,3
Viscosity index	121	98	90
Density at 200C, kg/m^3	876,3	894,4	912,6
Refractive index n^{20}D	1,4840	1,49140	1,5040
Molecular weight	361	400	444
Solidification temperature, ^{0}C	-18	-16	-16

Additive compositions. If the quality of raw materials and the conditions for its purification are not satisfactory enough, then in order to obtain the base of the optimal chemical composition and commercial oils of the required brands, it is necessary to change the composition of the additive composition.

Thus, the composition usually adopted for the production of oil of the M-12G type turned out to be ineffective in the base oil of the M-12 Ferghana refinery. This base, due to insufficiently deep purification with phenol, was characterized by an increased content of medium aromatic hydrocarbons (19.9% by weight) and resins (3.1% by weight). According to laboratory evaluation (11), the replacement of alkyl salicylate Detersol – 140 with an alkylphenolate additive Ferad and dithiophosphate DF-11 at the VNII NP did not give positive results. -354(Table 3).

Table 3

M-12 base oil with additive composition	Indicators after thermocatalytic oxidation		
	Optical density	Increase in viscosity at 40^{0}C	Weight loss of lead plates,%
1.5% Detersol-140 + 3% KN + 2.2% DF-11+3.2% S-5 A	0,46	76	7,7
1.5% Detersol-140+3% KN+ 2.2% DF-11+3.2% S 5 A ++0.5% Farad	0,44	81	7,4
8% Lubrizol-4970 +0.15% Lubrizol-1395	0,39	30	6,7
8% Lubrizol-4970 +0.15% Lubrizol-1395 +,05% Ferad	0,29	24	4,4

And only the use of the Lubrizol – 4970 package with Lubrizol – 1395 zinc dithiophosphate in combination with the Ferad additive, which has a higher reactivity in neutralizing oxidation products than the introduced package, made it possible to obtain M-12G engine oil, similar in quality to oil prepared on a better purified base.

Such a way is justified when the variability of the composition of oils and the insufficient content of hydrocarbons desirable for oils in them limit the possibility of obtaining a base of satisfactory quality.

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