LITERATURE CITED

1. V. F. Bolshakov, Internat. Shipowners Assoc. Bull., No. 354, 4-19 (1985).
2. E. D. Radchenko and G. A. Terent'ev, Khim. Tekhnol. Topl. Masel, No. 6, 2-4 (1984).
3. Z. I. Syunyaev, Khim. Tekhnol. Topl. Masel, No. 8, 5-7 (1986).
4. Z. I. Syunyaev (editor), Petroleum Chemistry [in Russian], Khimiya, Moscow-Leningrad (1984).
5. N. K. Kondrasheva, O. I. Rogacheva, and E. A. Maslovskaya, Neftepererab. Neftekhim., No. 5, 12-14 (1988).
6. N. K. Kondrasheva and E. A. Maslovskaya, Khim. Tekhnol. Topl. Masel, No. 2, 22-24 (1989).
7. P. L. Ol'kov, V. S. Gorelov, O. I. Rogacheva, et al., Khim. Tekhnol. Topl. Masel, No. 8, 36-38 (1981).
8. P. L. Ol'kov, V. S. Gorelov, O. I. Rogacheva, et al., Neft' Gaz, No. 5, 45-47 (1985).
9. O. I. Rogacheva, Candidate's Dissertation [in Russian], UNI, Ufa (1971).
10. O. V. Rogacheva, Candidate's Dissertation [in Russian], UNI, Ufa (1979).
11. S. R. Sergienko, B. A. Taimova, and E. I. Talalaev, High-molecular Nonhydrocarbon Compounds of Petroleum [in Russian], Nauka, Moscow (1979).
12. N. K. Kondrasheva, Candidate's Dissertation [in Russian], MINKh and GP im. I. M. Gubkina, Moscow (1982).

STABILIZATION OF LIGHT CATALYTIC GASOIL

A. M. Danilov, A. A. Selyagina, N. N. Demina,
T. N. Mitusova, I. Ya. Perezhigina, and
A. M. Senekina

UDC 665.7.035.5

The expanded role of catalytic cracking in the fuel balance has brought about an increase in the relative amount of middle distillates from secondary processing. These products, because of low octane number and unsatisfactory chemical and thermooxidative stability, are commonly used as components of furnace oils, marine fuels, and gas-turbine fuels; such use is never advantageous from the economic standpoint. Increasing emphasis is being placed on the utilization of light catalytic gasoil (LCGO) as a component of diesel fuel [1-3]. In this connection, it is of interest to investigate the stability of LCGO and its blends with straight-run diesel fuel (SDF).

The formation of precipitate and resins in unstable middle distillates very often fails to follow the laws of free-radical oxidation [4] that had been thoroughly studied in the example of gasolines and naphthas; from this point of view, the behavior of unstable middle distillates is a matter of independent scientific interest. Moreover, results obtained in studies of the stability of products obtained in destructive processing of petroleum feedstocks may be useful in investigating the extremely unstable hydrocarbon fractions obtained from nonpetroleum sources, for example by the liquefaction of coals and oil shales. Within the visible future, these products will find application as fuel components.

The stability of LCGO from the G-43-107 cat cracker at the Moscow Petroleum Refinery, alone and in blends with SDF, were investigated by heating fuel samples for 16 h at 100°C in air in the presence of a copper strip. This test method is included in the set of methods for qualification testing of diesel fuels [5]. After oxidation, the fuel sample is analyzed to determine the quantity of insoluble precipitate, acidity, existent gum content, and color (TsNT colorimeter).

Tests were performed on three samples of LCGO taken from the cat cracker at different times. The characteristics of these LCGO samples and the SDF sample are given in Table 1. A distinctive feature of the LCGO is its high content of aromatic compounds, amounting to 60-80%. At the same time, the concentration of unsaturated hydrocarbons, as determined by iodine number, is comparatively low. The LCGO differs from the SDF in content of bicyclic and tricyclic aromatic hydrocarbons. For example, the content of naphthalene derivatives in the

---

Élektrogorsk Branch, All-Union Scientific-Research Institute for Petroleum Processing.

Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 11, pp. 9-11, November, 1989.

0009-3092/89/1112-0535$12.50

TABLE 1

Index	LCGO			SDF
	sample 1	sample 2	sample 3	
Density at 20°C, kg/m^3	902	916	924	845
Cetane number	17	17	16	—
Distillation, °C				
IBP	190	162	175	198
10 %	210	198	175	198
50 %	234	235	242	282
EP (and yield, %)	296(98)	298(98,5)	287(98,5)	360(91)
Viscosity at 20°C, mm^2/sec	2,6	2,8	2,6	5,5
Temperature, °C				
solid point	−48	−50	−46	−8
limiting filterability	−39	−39	−37	−1
cloud point	−33	−28	−28	−1
Content				
sulfur, %	0,72	0,47	0,89	0,69
existent gum, mg/100 ml	—	83	30	—
Acidity, mg KOH/100 ml	1,2	0,54	1,27	1,9
Iodine number, g I$_2$/100 g	9,2	4,9	6,7	2,2
Ash	None			
Carbon residue of 10% bottoms, %	0,36	0,34	0,38	0,04
Filterability factor	1,4	1,6	1,3	1,2
Hydrocarbon group composition, %				
paraffins	—	6	2	16
isoparaffins and naphthenes	—	32	19	60
aromatics	—	62	79	24
monocyclic	—	30	34	18
bicyclic	—	30	42	5
tricyclic	—	2	3	1

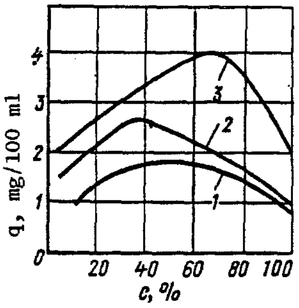

Fig. 1

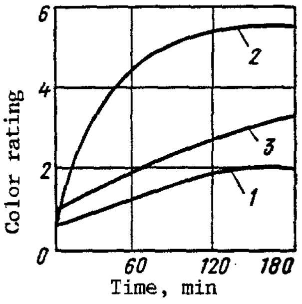

Fig. 2

Fig. 1. Quantity of precipitate q as a function of concentration c of LCGO in blend with SDF (curve numbering corresponds to LCGO sample numbers in Table 1).

Fig. 2. Change in fuel color during storage: 1) SDF; 2) LCGO; 3) blend of 30% LCGO and 70% SDF.

TABLE 2

Blend of 30% LCGO (sample 3) with 70% SDF	Quantity of precipitate,* mg/100 ml	Existent gum content, mg/100 ml	Color, TsNT units**
Storage in light			
Without additive	7,3	82	3,5
With additive			
ionol	7,0	90	3,5
MBI	3,1	66	3,5
Storage in dark			
Without additive	1,2	40	2,5
With additive			
ionol	1,3	38	2,5
MBI	1,0	34	2,5

---

*The term "precipitate" as used in this article probably represents the total of insoluble gum and the "precipitate" as defined in the ASTM method - Translator.

**Similar to NPA color - Translator.

LCGO is 6-8 times that in the SDF; for phenanthrene derivatives, the ratio is 2-3. This feature is undoubtedly an important factor in determining the formation of resinous predecessors of precipitate and the formation of the precipitate itself.

The greatest quantity of precipitate is formed in blends containing 35-70% LCGO with the SDF (Fig. 1). The amount of insoluble precipitate formed in the LCGO is less than in its blends with the SDF, and sometimes even less than in the SDF itself. The formation of precipitates in the process of coagulating molecules of predecessors is quite probably hindered in media with high contents of aromatic and naphthenic hydrocarbons [6]. But this does not mean that any smaller amounts of oxidation products are formed in the LCGO. Evidence for this statement may be found in the rapid darkening of LCGO samples during storage and heating. In Fig. 2 we show the timewise changes in color of LCGO and SDF samples during storage in diffuse light at room temperature.

In Table 2 we present results obtained on a blend of 30% LCGO (Sample 3) and 70% SDF, containing 0.01% additive, after storage for 120 days at room temperature, in the dark or in diffuse light. Exposure to light has a significant influence on fuel stability, giving an increase in the amount of precipitate by a factor of 3-6, a twofold increase in the existent gum content, and darkening of the product. The addition of Ionol [2,6-di-tert-butyl-4-methylphenol] has no effect on the behavior of the fuel in storage. Addition of the Mannich base of Ionol (MBI) results in a smaller quantity of sediment, but gives practically no change in the existent gum content or the color of the fuel after storage. Thus we see that inhibitors of free-radical oxidation are ineffective in the LCGO.

The information reported in the literature on precipitate formation in LCGO is quite contradictory. Some of the information supports the results we have obtained, whereas other data indicate severe precipitate formation in LCGO [2, 3]. The reason for these differences may be found in specific features of the composition of the samples tested, particularly in the content of heteroatomic impurities. It does not appear that any detailed or comprehensive studies are required to explain these differences.

Still unclear is the mechanism through which the predecessors of the precipitate are formed; here we define as predecessors the high-molecular-weight products of fuel component conversions that are susceptible to coagulation into a solid phase. The precipitate predecessors are probably formed not only in oxidative processes, but also in processes of polymerization and polycondensation of unstable components of the fuel. In [8], for example, it was reported that the quantity of oxygen absorbed shows no correlation whatever with the quantity of precipitate. This statement is supported by results of elemental analysis of the test samples: The content of heteroatoms in the oxidation products is far higher than in the original fuels. For example, the LCGO contained 89.84% C, 9.20% H, 0.07% N, and 0.89% S; the precipitate obtained after tests on the LCGO contains 77.5% C, 6.45% H, 3.33% N, 2.62% S, and 10.1% O (by difference).

In practice, three approaches may be used in stabilizing secondary middle distillates [1-4]: caustic washing, hydrotreating, and the use of additives. We have investigated hydrotreating and the use of additives. In our experiments, the LCGO (Sample 3) and its blend with the SDF were hydrotreated on GKD-202 catalyst under a total pressure of 4 MPa, reactor

TABLE 3

Index	LCGO (sample 3)		Blend of 30% LCGO with 70% SDF	
	before hydro-treating	after hydro-treating	before hydro-treating	after-hydro-treating
Density, kg/m^3	924	913	861	855
Acidity, mg KOH/100 ml	1,3	0,4	1,8	1,1
Sulfur content, %	0,89	0,19	0,73	0,19
Iodine number, g I_2/100 g	6,7	3,6	3,1	2,9
Chemical stability				
precipitate, mg/100 ml	1,25	—	1,53	1,1
color, TsNT units	6,0	2,0	2,5	1,5
Content of aromatic hydrocarbons, %	64,7	57,0	—	—
monocyclic	31,4	41,3	—	—
bicyclic	30,8	13,2	—	—
tricyclic	2,5	2,5	—	—

TABLE 4

Blend of 30% LCGO (sample 3) with 70% SDF	Quantity of precipitate, mg/100 ml	Existent gum content, mg/100 ml
Without additive	3,2	58
With additive		
Ionol	3,5	45
FCh-16	4,1	44
Agidol-12	2,1	49
MBI	1,6	29
A*	1,2	37
B*	1,3	30

---

*Experimental samples.

temperature 380-400°C, feedstock space velocity 3 or 6 h^{-1}, and hydrogen-rich gas circulation ratio 300 liters/liter. We found that hydrotreating increases the stability of the LCGO (Table 3), reducing the precipitate formation by a factor of 1.5 and improving the color. The increase in stability can probably be attributed to the decrease in quantities of undesirable impurities in the LCGO. For example, the hydrotreating lowers the sulfur content by a factor of 4-5 and the acidity by a factor of 1.5-3. It also lowers the content of unsaturated hydrocarbons.

Hydrotreating produces a change in the group composition of the fuels, primarily a decrease in the quantity of aromatic hydrocarbons. This is indicated indirectly by a certain increase in cetane number and decrease in density. The solid point, cloud point, and limiting filterability temperature are somewhat higher for the hydrotreated fractions. The UV spectra of the samples indicate that the naphthalene hydrocarbons are highly subject to hydrogenation: The content of these hydrocarbons decreases by a factor of 2-3. Along with this, there is an increase in the concentration of monocyclic aromatic hydrocarbons. The changes in group composition undoubtedly affect the precipitate formation in the fuels, but the character and degree of this effect will require special studies.

The additives used in other countries to stabilize middle distillates may contain antioxidants, metal deactivators, dispersants, and so-called stabilizers [1]. The role of the stabilizers consists of neutralizing acidic impurities (or oxidation products) that initiate the formation of gum and precipitate. Tertiary aliphatic amines are commonly used as stabilizers. As regards dispersants, they are intended to retard the coagulation of the precipitate predecessors that results in formation of a solid phase.

In the USSR, where stable straight-run fractions have been available for many years for the production of diesel fuels, no additives of these types are yet available. The antioxidants used to stabilize automotive gasolines, such as Ionol or FCh-16, are unsuitable for diesel fuels. The results from tests of some of these additives at a concentration of 0.01% in a blend of 30% LCGO (Sample 3) with 70% SDF are presented in Table 4. Of the additives commercially produced in the USSR, the most effective is the MBI, probably because of the presence of a tertiary amine group in its molecule. A weak stabilizing effect is observed for the Agidol-12, which is a blend containing a certain amount of the MBI.

Effective stabilizing additives may be formulated from phenolic antioxidants and certain special-purpose additives, particularly dispersants. Preliminary tests have indicated excellent possibilities in working along these lines (see Table 4, Samples A and B). The additives can be formulated from components produced commercially in the USSR.

LITERATURE CITED

1. M. W. Schrepfer, R. J. Arnold, and C. A. Stansky, Oil Gas J., 82, No. 3, 79-84 (1984).
2. K. Kanariev, A. Ivanov, and Z. Kutsarova, Khim. Ind. (Sofia), 58, No. 8, 346-348 (1986).
3. A. A. Gureev, T. V. Palichev, and D. M. Minkov, Khim. Tekhnol. Topl. Masel, No. 10, 12-13 (1987).
4. A. M. Danilov, Khim. Tekhnol. Topl. Masel, No. 3, 42-44 (1987).
5. A. A. Gureev, E. P. Seregin, and V. S. Azev, Qualification Test Methods for Petroleum Fuels [in Russian], Khimiya, Moscow (1984).
6. G. F. Bol'shakov, Physicochemical Principles of Precipitate Formation in Jet Fuels [in Russian], Khimiya, Moscow (1972).
7. A. A. Gureev and G. B. Prigul'skii, Khim. Tekhnol. Topl. Masel, No. 6, 16-18 (1985).
8. F. R. Mayo and B. Y. Lan, Ind. Eng. Chem., Prod. Res. Dev., 25, No. 2, 333-348 (1986).

TREATMENT OF POLYMER-COMPOUNDED HYDRAULIC OILS BY ULTRAFILTRATION

V. A. Kulikova, A. I. Bukhter, L. K. Davidyan,
G. S. Krasnov, and Yu. A. Avdonin

UDC 66.067:665.544

Polymer-compounded oils have been finding more and more applications in the lubrication of components of vehicles and mechanisms, and also as the working fluids in various hydraulic systems. These products are formulated from a low-viscosity oil base plus polymeric additives such as polymethacrylates, Oktol [low-molecular-weight polybutylenes], Vinipol [poly(vinyl n-butyl ether)]. Such oils are characterized by good viscosity–temperature properties at low and high temperatures. After these oils have been in service for a certain time, they are drained and discarded as unsuitable for further use.

There is no economic commercial method for reclaiming polymer-compounded oils. One method of oil reclaiming is treatment with sulfuric acid followed by neutralization. However, this results in the formation of large amounts of waste materials that present a problem in environmental pollution. Oil reclaiming by such methods as deasphalting, vacuum distillation, hydrotreating, or contact-treating with bleaching clay is quite complex and costly in terms of energy requirements and capital investment [1].

In many branches of industry, treatment methods using polymeric membranes have come into use. The principles of membrane separation technology are described in [2]. According to data reported from other countries [3], ultrafiltration using "nuclear" membranes is one of the promising methods of oil reclaiming. The mechanical design of equipment for this process is simple, the energy costs are low, and, as a consequence, the process is very economical. Distinctive features of nuclear membranes are the regular cylindrical form of the pores and the extremely narrow size distribution of the pores [4].

We have applied ultrafiltration to the reclamation of used AMG-10 oil. This oil is intended for operation at ambient temperatures from -66°C to +55°C. It is prepared from a low-viscosity, low-power petroleum base stock (a distillate produced from the kerosine cut of Balakhany crude by severe treatment with sulfuric acid) plus a polymeric V. I. improver, an antioxidant, and a dye. The V. I. improver is Vinipol VB-2 (a polymer of vinyl butyl ether with a molecular weight of 15,000-20,000). The base stock of the AMG-10 oil has a viscosity

---

Ryazan' Pilot Plant, All-Union Scientific-Research Institute for Petroleum Processing. dzerzhinsk Branch, State Scientific-Research and Design Institute of the Nitrogen Industry and Products of Organic Synthesis. Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 11, pp. 11-13, November, 1989.

0009-3092/89/1112-0539$12.50