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SHALE-OIL-DERIVED ADDITIVES FOR FUEL OILS

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Studies have shown that the oxidation, wearing, and anticorrosive properties of shale oil as an additive to liquid fuels and oils enable to improve the conditions of their use. Studies conducted by Institute of Oil Shale have shown that it is possible, on the basis of shale oil produced by Viru Keemia Grupp AS (Viru Chemistry Group Ltd.) and, particularly, on the basis of its fractions 230–320 and 320–360 °C to produce efficient and stable additives for liquid fuels to improve their combustion and storage properties. In the production of additives from shale oil the prerequisite taken into account is its complexity of composition and high concentration of neutral and phenolic oxygen compounds. Additives produced from shale oil have multifunctional properties which enable to improve operational data of liquid fuels and to increase the power of diesel engines and boilers.

Introduction

This study is aimed at the extension of spheres of application of main oil shale products, such as distillate fractions of shale oil and improvement of economic data of oil shale processing industry. Ways of more valuable application should be found for shale oil, including more profitable uses of its compounds.

The shale oil produced by *Viru Keemia Grupp AS* (*Viru Chemistry Group* Ltd.) (former *Viru Õlitööstus AS* ((*Viru Oil Industry* Ltd.)) has an extremely complex composition (over 400 compounds). It consists mainly of three compound groups – hydrocarbons (~40 %), phenolic compounds (~30 %) and neutral oxygen compounds (~30 %). The majority of phenolic compounds is represented by alkyl resorcinols. Alkyl resorcinols with long side chains (C_7–C_{12}) and especially neutral oxygen compounds present in the oil have shown good antioxidant as well as wear and corrosion-resistant properties when used as additives to fuels and oils [1].

Because of the unique composition of shale oil and high reactivity of its components it was possible to develop new additives improving the combus-

tion and storage properties of liquid fuels. Development was basically conducted in two directions – production of magnesium and manganese-containing additives and production of ash-free additives. At application their multifunctional properties improve the operational data of liquid fuels. Usually additives having the same functions are produced by synthesis or from artificially made blends of complex composition, for whose dilution volatile organic solvents are needed [2–4]. According to advertising, multifunctional additives are produced by a number of chemical companies (*Morbac*, *BASF*, *Exxon-Nalko*, *Lennart Hojer AB*, *Pari*, etc.).

As the objective of this study practical evolution of technologies for the production of additives for liquid fuels was set up, as well as determination of technical properties of products obtained and check of the application efficiency of liquid fuels with these additives (0.03–0.2 %) under operation conditions (boiler houses and diesel engines).

Technical Properties of Shale Oil Fractions 230–320 and 320–360 °C

Thermal decomposition (retorting) of oil shale in retort stations yields light-medium oil (55 %) and heavy oil (45 %) which is, after a thorough preparation and cleaning, directed to distillation. By distillation mostly two cuts are taken – 230–320 and 320–360 °C with the yields from the initial raw oil 16–18 and 14–16 %, respectively. The yield and composition of the latter depend on the application of distillation residue, for example, for the produc-

Table 1. **Properties of Shale Oil Fractions (Produced in March 2000 by *Viru Oil Industry* Ltd.)**

Properties	Fraction 230–320 °C	Fraction 320–360 °C
Density at 15 °C, kg/m^3	985	1036
Water, %	no	no
Ash, %	no	no
Mechanical solids, %	no	no
Pour point, °C	–35	–9
Flash point (open cup), °C	110	152
Kinematic viscosity at 80 °C, mm^2/s	2.3	30
Engler specific viscosity at 80 °C, degrees	1.13	3.8
Distillation, vol. %:		
initial boiling point, °C	225	290
to 240 °C	6	–
to 260 °C	30	–
to 280 °C	78	–
to 300 °C	92 (94)	4
to 320 °C	–	10
to 340 °C	–	26
to 360 °C	–	64 (78)
Average molecule weight	233	329

tion of coke for carbon electrodes. The properties of fractions applied for the production of additives is given in Table 1. Production of additives is feasible because of the presence of long side chain (C_7–C_{12}) phenolic compounds (alkyl resorcinols) and aromatic neutral oxygen compounds with disperging and antioxidant abilities. They are also used for dilution, stabilization and improvement of cold resistance of heavy petroleum oils.

Production of Additives

Shale oil fractions 230–320 and 320–360 °C were used as initial raw material for the production of SOMAG and SOMAN additives containing metal (Mg, Mn) compounds. For the production of these additives laboratory instructions, flow charts and material balances were developed. The materials containing magnesium and manganese were prepared and used both separately and in blends. The SOMAN additive was produced in laboratory (in 15 l reactor) and using a pilot-scale plant (1.2 m^3 reactor) of *Viru Liimid AS* (*Viru Glue* Ltd.).

The experimental tests showed the possibility of producing the SOMAN additive by batch technology.

For the production of the ash-free SO-2E additive for diesel fuels shale oil fraction 320–360 °C was used. This fraction contains high-polar alkyl resorcinols with long-side chains and neutral oxygen compounds. Laboratory instructions were developed and some twenty or thirty samples of SO-2E additive produced. On the basis of the data obtained a technological chart was developed for the 15 l reactor. During experiments the flow chart and the material balance were specified, and larger test samples were produced for testing in diesel engines. It was shown that the SO-2E additive can also be produced by batch technology.

Table 2. **Technical Properties of Additive Samples**

Properties	SOMAG*	SOMAN*	SOMAN**
Appeareance	Dark brown flowing liquid		
Ash, %	1.4–1.8	4.3–4.5	5.5
Acid number, mg KOH/g	11.3–20.0	11.8–12.0	22.0
Water, %	0.4–0.8	2.9–5.6	3.2
Flash point (open cup), °C	107	106–112	112
Density at 15 °C, kg/m^3	960–990	1055–1070	1115–1200
Kinematic viscosity, mm^2/s:			
at 50 °C	–	465	699
at 80 °C	–	168	183
Magnesium content, %	0.5–0.9	–	–
Manganese content, %	–	1.9–2.4	2.5
Pour point, ° C	<–15	<–15	<–15

* Laboratory experiments.
** Pilot-scale test.

Technical Properties of the SOMAG and SOMAN Additives for Fuel Oils

Technical properties of additives produced based on metal-containing shale oil fractions are given in Table 2.

Application of the SOMAN Additive to Fuel Oils in Boiler Houses

The SOMAN additive was successfully applied in boiler houses located in Tartu (*Tamme Soojus*), at Kehra (*Alto Soojus OÜ*) and Saue (*Termo AS*). Some 0.05 to 0.1 % of the additive was applied to fuel oil. Some 600 kg of the additive was applied in boiler houses.

Positive qualitative results were obtained. As a result of firing fuel oils the formation of soot was reduced, the more homogeneous composition of the oil led to good flame stability. By firing during a period about twice as long as usual, no additional soot formation in burners and on the tubes inside the boiler was reported. Consequently, by introducing the SOMAN additive to fuel oil, the latter tends to be more completely combusted, and the efficiency of heating improved.

Properties of the SO-2E Additive for Diesel Fuel

Properties of the SO-2E additive produced in a separatory funnel and by pilot facilities are given in Table 3. The products of three cycles produced in pilot facilities were mixed, and the average properties are given.

Table 3. **Properties of the SO-2E Additive Produced from Shale Oil**

Technical properties	Laboratory samples	Pilot test
Appearance	Dark brown flowing liquid	
Ash, %	Traces	Traces
Water, %	1.5–1.6	0.5
Acid number, mg KOH/g	1.5–1.8	1.8
Flash point (open cup), °C	80–110	100
Density at 15 °C, kg/m^3	1012–1023	1012
Kinematic viscosity, mm^2/s:		
at 20 °C	295–305	312
at 25 °C	195–210	199
Average molecular weight	330–342	336
Yield from shale oil fraction 320–360 °C	69	79

Efficiency Assessment of the SO-2E Additive Applied to Diesel Fuel

By 0.1 % of the SO-2E additive applied to diesel fuel, a 2.1 % increase in kinematic viscosity and a 1.8 % improvement of lubricity resulted. The Gardner colour was determined to be darker by one unit only. The operational data of stand engines fired with diesel fuel containing 0.1 % additive are given in Table 4.

Table 4. **Improvement of Efficiency by Applying SO-2E Additive to Summer Diesel Fuel**

Automobile (engine)	Reduction of emissions, %			Reduction of noise caused by pump, %
	CO	Hydrocarbons	NO_x	
BMW 324 D, 86 HP	15.5	22.0	2.3	1.8
Nissan 2.5 D, 110 HP	3.7	5.2	2.4	3.6
Scania 12 TD, 540 HP	1.1	3.4	0.2	2.5

By testing the additive in a bus equipped with *Karosa B731*-type diesel engine (after a run of 50,000 km), a 5-6 % saving of fuel and a 27.8 % reduction of exhaust gases (CO, hydrocarbons, etc.) was reached. No soot formation was visually observed.

Conclusions

1. Shale oil fractions commercially produced by *Viru Chemistry Group* Ltd. are suitable for production of additives. The SOMAN additive for boiler fuel can be produced from fractions 230–320 and 320–360 °C, and the SO-2E additive for light fuel oils and diesel fuel oil from the fraction 320–360 °C.
2. Semi-commercial production of test quantities of the SOMAN additive on an experimental unit of *Viru Chemistry Group* Ltd. and preparation of SO-2E additive on the laboratory facilities of the institute indicated possibilities of using the batch process at *Viru Chemistry Group* Ltd.
3. Laboratory samples and enlarged quantities of the additives of the same type were produced and their similar technical properties were demonstrated confirming the possibility of stable quality at the production.
4. Additives produced from shale oil are multifunctional enabling to improve the operating data of many liquid fuels and increase the performance rate of diesel engines and boilers to a level analogous to other known additives.
5. The SOMAN additive homogenizes the composition of boiler fuels and decelerates their separation in oil storage tanks.

6. The SO-2E additive for ash-free diesel fuel reduces fuel consumption and emission of environment polluting waste products (smoke, unburnt hydrocarbons, CO and soot), reduces gum formation in initial diesel fuel and keeps the jets of the burners clean.

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