CURRENT PROBLEMS

NAPHTHENIC ACIDS AS ANTIWEAR ADDITIVES FOR JET FUELS

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One of the ways in which the antiwear properties of jet fuels can be improved is the use of lubricity agents, otherwise known as antiwear additives. Among the various compounds that have antiwear properties in these fuels, naphthenic acids merit special attention. These are alicyclic carboxylic acids, in most cases monobasic, with five- and six-membered carbon rings; they have the general formula $R(CH_2)_nCOOH$, where $R$ is a naphthene radical.

Natural naphthenic acids consist mainly of acids of the cyclopentane series, beginning with the simplest, in particular cyclopentylacetic acid. The lower naphthenic acids are monocyclic; the higher acids, beginning with C$_{13}$, are bicyclic and polycyclic. Naphthenic acids of the cyclohexane series are encountered less frequently; they may be found, for example, in Baku, California, and Sakhalin crudes.

The most widely used method for obtaining naphthenic acids is the treatment of light distillates, lube distillates, and diesel fuels [1, 2]. The standard GOST 13302–77 establishes several grades of naphthenic acids, depending on the raw material and the production technology: distilled naphthenic acids, obtained by vacuum distillation of the petroleum acids recovered from light petroleum products; technical naphthenic acids (*asidol*™ A-1 and A-2), obtained by decomposing the sodium salts of petroleum acids recovered in the treatment of lube distillates, or recovered from light distillate products; *asidol–mylonaft,*™ a mixture of petroleum acids and their sodium salts, obtained by partial decomposition of the sodium salts of petroleum acids by treatment with sulfuric acid; and mylonaft, the sodium salts of petroleum acids.

In certain refineries, for example the Krasnodar, Ukhta, and Komsomol' refineries, in the caustic treatment of diesel fuels and lube distillates, mylonaft containing petroleum acids is also obtained as a byproduct or waste material. At the Krasnodar refinery, 800 tonnes of mylonaft are obtained each year; this material does not meet the quality requirement of GOST 13302–77 with respect to the acid number, which is 210 instead of the required 220 mg KOH/g. It is used as a starting material in producing sodium naphthenate in manufacturing the inhibitor VNITOL. At the Ukhta refinery, in the caustic treatment of diesel fuel (2-3 million tonnes/yr), a caustic waste containing 87 % water is formed. Preliminary data indicate that this waste material is produced in amount of 40,000 tonnes/yr.

Various methods are known for determining the content of naphthenic acids in caustic wastes [3]. One of these methods calls for deoiling caustic wastes containing various amounts of mylonaft by means of a binary solvent such as a mixture of methyl ethyl ketone and extraction naphtha in a ratio from 1:1 to 1:2. Such treatment eliminates the problem of emulsion formation. After mixing and settling, the two layers are separated. The upper layer consists of a solution of unsaponifiable substances in the solvent, and the lower layer is an aqueous solution of deoiled mylonaft with a small amount of methyl ethyl ketone. The unsaponifiables, after driving off the solvent, are recycled; the aqueous solution of mylonaft is concentrated by precipitation or is subjected to additional azeotropic distillation with extraction by naphtha. Another method that has been proposed for analyzing caustic wastes is based on a ternary titration with two indicators – phenolphthalein and methyl orange.

The work reported here was aimed at the utilization of wastes containing naphthenic acids, with subsequent use of these materials as the basis for development of additives to improve the antiwear properties of jet fuels. This required the development of a method for recovering naphthenic acids from various types of mylonaft, a determination of whether the acids

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*The Russian terms "asidol" and "mylonaft" denote petroleum naphthenic acids and sodium naphthenates, respectively – Translator.*
Thus obtained would meet the quality requirements of GOST 13302-77, and an evaluation of the effectiveness of these materials as antiwear additives for jet fuels.

We investigated commercial samples of mylonaft obtained at the Krasnodar and Komsomol’ refineries (samples 1 and 2, respectively). In developing a procedure for recovering naphthenic acids under laboratory conditions, we used as the primary reagents water, BR-1 solvent naphtha, and sulfuric acid. A simplified flow chart of the unit for recovering naphthenic acids is shown in Fig. 1.

The calculated quantity of mylonaft was charged to a glass mixing vessel with a slow-speed stirrer, where it was mixed with water for a period of 0.5-1 h at 50°C. Then, BR-1 naphtha was added to the mixture, and stirring was continued for 0.5-1 h. At the end of the stirring period, the mixture was allowed to settle in the mixing vessel for 1 h. The lower layer, consisting of a solution of mylonaft in water, was drawn into the tank 5; the upper layer, consisting of a solution of oil in naphtha, was drawn into tank 2, where it was checked for the presence of oil. If oil was detected, the mixture was fed into tank 3 for utilization. If no oil was detected, the mixture was fed to tank 4, serving as a receiving tank for the spent solvent naphtha.

The operation for oil extraction was repeated until the naphtha layer was completely free of oil. Then a 20% sulfuric acid solution was charged to the mixture in amount calculated to give a 2:1 volume ratio of mylonaft to sulfuric acid; after stirring for 0.5 h, solvent naphtha was added in amount required to give a 1:1 ratio of naphtha to sulfuric acid. After stirring, the mixture was left to settle for about 6 h. The lower layer was drawn off into the tank 3.

The naphthenic acid solution remaining in the mixer was transferred to the vaporizer 6 to drive off the solvent at a temperature no higher than 140°C. The naphthenic acids passed into the receiver 7, from which they were fed to the vaporizer for vacuum distillation. The yield of naphthenic acids was 75-80%. The purified naphthenic acids were directed to the receiver 8, from which a sample was taken for analysis to determine conformance with GOST 13302-77.

In Table 1 we present results obtained in evaluations of the naphthenic acid quality. Sample 1 meets all requirements of GOST 13302-77, but sample 2 does not meet the requirements for color or acid number. Therefore, sample 1 was taken for the subsequent tests of the naphthenic acids as a jet fuel additive.

The tests were performed in a stand with a friction test section consisting of a part of an NR-21F2 aircraft pump assembly. This method, which is included in the set of methods for qualification testing of fuels for gas turbine engines, is intended for accelerated laboratory evaluations of the antiwear properties of jet fuels. It consists essentially of pumping 50 liters of test fuel, preheated to 50°C, through the test section (plunger pump of the NR-21F2 fuel pump assembly), with subsequent measurement of the wear scar diameter on control balls installed in three plungers.

We evaluated the naphthenic acids (NA) obtained from mylonaft produced at the Krasnodar refinery. The tests were performed in hydrotreated fuels differing in their original antiwear properties. For comparison, we tested these same fuel samples with distilled naphthenic acids (DNA) from Baku crudes, which are used as an antiwear additive in RT fuel [thermally stable jet fuel] conforming to GOST 10227. Also tested for comparison was the imported additive Hitec-580, which is approved for use and is known to have an antiwear effect. The results of these tests are presented in Table 2.