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CORROSION INHIBITING ADDITIVES FOR
SULFUR-CONTAINING FUELS

Yu. Shekhter, et al

Army Foreign Science and Technology Center
Charlottesville, Virginia

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220 SEVENTH STREET NE.
CHARLOTTESVILLE, VIRGINIA 22901



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AUTHOR: Shekhter, Yu., Yevstratova, N. I., Cherepenina, V. N.

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REQUESTOR: AMXBR

TRANSLATOR: Leo Kanner Associates, Redwood City, California (DPS)

ABSTRACT:

Performance of numerous corrosion inhibitors was reported and discussed. Various amine corrosion inhibitors were synthesized and tested, and they proved to be less effective than sulfonates or nitrated products. Various ammonium salts of acid, oil-soluble products were synthesized and tested by the authors, some of them proving to be quite effective. Various combined additives, produced by mixing acid sulfo and nitro products, turn out to be the most effective corrosion inhibitors and are widely used at present.

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Corrosiveness of fuels under storage conditions depends on their antioxidant stability.

Antioxidants are added to fuels to stabilize them: n-oxydiphenylamines, phenols (FI-16), 2,6 isobutyl - 4-methylphenol(ionol) [1,2], 2,2-methylene-bis-(4-methyl-6-isobutyl phenol).

The purpose of such antioxidants is to prevent formation of oxidation products in gasoline. Such substances are not corrosion inhibitors, i.e., they do not protect metal from destruction in the presence of water.

During prolonged storage of fuelled motor vehicles, conditions are created for separation of water dissolved in the fuel in the form of microdrops, settling on parts of the fuel equipment. During storage of fuel in tanks, as a result of average daily temperature fluctuations, condensation of water vapors from the air on the fuel surface can take place.

In all these cases, corrosion of the metal develops, not only as a result of the reaction of water emulsified with or dissolved in fuel, but the reactivity of the sulfur compounds in the fuel; mercaptans, disulfides, sulfides also increases sharply in the presence of water [1]. In connection with this, in addition to antioxidant and anticorrosion additives, oil-soluble corrosion inhibitors

(antirust additives), protecting the metal from corrosion under precisely these conditions, must be added to the fuel.

Oil-soluble sulfonates of various metals and nitrated oils have been proposed as additive-inhibitors to sulfur-containing diesel fuels [3-5].

It has been determined that medium-molecular-weight calcium sulfide from AS-6 oil (KSK) has the best inhibitor properties in fuels of various compositions.

Petroleum sulfonates, besides an inhibiting effect, improve the fuel combustion process and sharply decrease the separation of sediments from them [6]. However, they have a high ash content; therefore, their addition to fuels is limited to hundredths of a percent. At higher concentrations, fuel combustion in the engine is accompanied by increased scale formation. Moreover, for technological reasons [4], oil-soluble sulfonates can be produced only in the form of 15-20% solutions in oil. In this manner, with introduction of 0.01% sulfonate to a fuel, (calculated on the active component), 0.05% mineral oil is introduced into it simultaneously. It is extremely difficult to separate the sulfonates from oil solutions in the form of powders or even 50-60% concentrates.

There is particular interest in use of nitro compounds, in particular, nitrated oils, as fuel corrosion inhibitors.

Oil-soluble nitro compounds are the most widespread additives to gasolines, kerosene, and diesel fuels [7,8].

It has been determined, as a result of testing on a special small-size unit, that the individual nitro compounds, nitromethane, hexanitroethane, tetranitromethane, as well as nitrated cracking gasoline with a 8.5% NO_2 content and nitrated isoethylene oxide, considerably increase the combustion rate of fuels [9]. It also has been determined that the active principle in these additives is the NO_2 group. Compounds containing two or more such groups, for example, dinitro

compounds or tetranitro compounds, gave the same effect, with their addition to fuel in considerably lower concentrations. Nitrated petroleum products [10] are anticorrosion additives and simultaneously improve the fuel combustion process. Nitrated oil, neutralized with a water solution of ammonia, decreases the corrosivity of sulfur-containing diesel fuels and it completely protects ferrous metals and considerably reduces corrosion of nonferrous metals at a concentration of 0.01% in fuel [3].

Salts of cyclo and dicyclohexylamine with synthetic fatty acids (SFA), of various fractions, from C_6 to C_{24} , have been proposed as corrosion inhibitors [11]. Salts of dicyclohexylamine (MCDA additive) [11] and the products of incomplete condensation of still residues of triethylamine and fatty acids [12] have demonstrated good results.

A large number of compounds, which are reaction products of organic acids, sulfo acids, polyamines or amino alcohols have been recommended [13,14].

Such additives are recommended for addition to fuels, in the amount of 0.005-1% and 1-25% to oils.

Thus, tests carried out showed that diesel fuel with a 1% amine sulfonate content protected steel in a humidity chamber for a period of 16 days, while fuel without additive gave corrosion after a few minutes, and fuel with 1% ammonium sulfonate protected metal for a period of 3 days [14].

The authors have tested the effectiveness of various corrosion inhibitors, by methods adopted for evaluation of inhibitors at the Neftegaz plant [3,4]. Tests were conducted in a G-4 heat and humidity chamber (hydrostat) and in water, using standard metal plates, 45 x 30 x 4 mm in size, prepared in the usual manner [3].

Comparative tests of additives as corrosion inhibitors were conducted in distilled water, with the additive (5%) dissolved in transformer oil (standard agent, standard). Metal plates covered with oil and inhibitor were placed in beakers of water, which were placed in a thermostat and were kept in it, at a temperature of 60°C, for a period of 8 hours. For the remaining time, the apparatus was cooled.

Tests with sulfur-containing diesel fuel (GOST 305-63)¹ were conducted in a heat and humidity chamber (hydrostat), at 20-40°C, and in beakers, at the "fuel-tap water" interface, at 20-60°C. 0.5% of the additive, based on the active component, was added to the fuel.

Under these test conditions in the chamber and in water, the sulfur-containing diesel fuel gives solid corrosion (10 points) after a few minutes.

Testing in the heat and humidity chamber and in water is more rigid than according to method [5].

We synthesized and tested oil-soluble amine corrosion inhibitors (see Table 1).

Nitration of oils and SFA was accomplished with 60% nitric acid, used in the amount of 30-50% of the product. Reduction was carried out with cast iron chips and hydrochloric acid, in the presence of catalysts, copper salts, at a temperature of 100°C.

Solubility of the resulting additives in fuel was determined at temperatures between -30 and +90°C. In this case, from 0.001 to 10% additive was added to the fuel.

Positive results on corrosion of steel 45 were obtained with reduced nitrated SFA and reduced nitrated oil. However, the amine corrosion inhibitors turned out to be less effective than the sulfonates or nitrated products (Table 2).

¹ [GOST--All-Union State Standard]

TABLE 1: RESULTS OF AMINE CORROSION INHIBITOR TESTS

Additive	External appearance and viscosity at 100°C, centistokes	Solubility in fuel	Alkalinity, mg KOH by bromophenol blue	Active component content, % of additive	Corrosion in points, steel 45 ¹		
					In water at 20-60°C, 5% additive in transformer oil (5 days)	At "water-diesel fuel" interface, 0.5% additive ² (3 days)	In heat and humidity chamber at 20-40°C, 0.5% additive in diesel fuel ² (3 days)
Diphenylamine	White crystalline powder	Complete	-	100	10	10	10
Condensation product of triethanolamine and SFA(C ₅ -C ₂₀)	Thick, unstable mass	Partial	30	100	0	5	3
Condensation product of diphenylamine and SFA (C ₅ -C ₂₀)	Same	Complete	15	100	0.3	10	4
Condensation product of dicyclohexylamine and SFA(C ₁₀ -C ₁₂)	"	Complete	40	100	5-6	10	8
Condensation product of oxidized petrolatum and triethanolamine	"	Partial, precipitate	72	100	0.1	2.5	0.6
Condensation product of oxidized petrolatum and dicyclohexylamine	"	Same	50	100	0.3	-	-
Salt of triethanolamine and oil-soluble sulfonic acids (volumetric reaction through calcium sulfonate)	Oil, 100-50	Complete	86	60	5	4	0.1

TABLE 1 (continued)

Additive	External appearance and viscosity at 100°C, centistokes	Solubility in fuel	Alkalinity, mg KOH by bromophenol blue	Active component content, % of additive	Corrosion in points, steel 45 ¹		
					In water at 20-60°C, 5% additive in transformer oil (5 days)	At "water-diesel fuel" interface, 0.5% additive ² (3 days)	In heat and humidity chamber at 20-40°C, 0.5% additive in diesel fuel ² (3 days)
Product of reduction of of nitrated SFA (C ₅ -C ₂₀)	Thick mass	Complete	8	100	0	-	-
Amine oil (reduced nitro oil)	Oil 100-16	"	15	10	8	0.6	0.1

¹10 points--continuous corrosion over entire surface of plate, in the form of dots or spots; 0 points--entire plate clean.

²Amount of additive based on active component.

Subsequent testing showed that amine corrosion inhibitors protect nonferrous metals, copper, copper alloys, cadmium-plated parts, poorly.

The amine corrosion inhibitors are anticorrosion additives, which, during combustion, evidently neutralize the sulfur oxides and other acid combustion products, as a result of formation of ammonia.

Ammonia itself, added to fuel [15], as well as various ammonia salts, have a similar neutralizing effect.

We synthesized and tested, as fuel additives, ammonium salts of acid, oil-soluble products--sulfo acids, nitrated oil, synthetic fatty acids (various fractions), oxidized petrolatum, nitrated SFA, nitrated alkylphenol and others. Some of these ammonium additives (see Table 2) turned out to be effective corrosion inhibitors. Nitrated oil, alkalinized with ammonia, proved to be highly effective.

TABLE 2: RESULTS OF TESTS OF CERTAIN CHEMICAL PRODUCTS AS CORROSION INHIBITORS

Additive	External appearance and viscosity at 100°C, centistokes	Solubility in fuel	Alkalinity, mg KOH by bromophenol blue	Active component content, % of additive	Corrosion in points ¹		
					In water at 20-60°C, 5% additive in transformer oil (5 days)	At "water-diesel fuel" interface, 0.5% additive ¹ (3 days)	In heat and humidity chamber at 20-40°C, 0.5% additive in diesel fuel ¹ (3 days)
Ionol--2,6-isobutyl-4-methylphenol	White crystalline powder	Complete	0	100	10	10	10
Preparation "22-46"--2,2-methylbis-(4 methyl-6-isobutyl phenol)	Same	Partial	0	100	10	10	10
"CSC"--calcium sulfonate concentrate	Brown liquid, 21	Complete	10	15	2.5	0	0
"ASC"--ammonium sulfonate concentrate	Same, 26	Same	2	15	0	1.5	0.5
Nitrated oil, alkalized with NH ₄ OH	Same, 15	"	5	10	5	0	0
SFA(C ₅ -C ₂₀), alkalized with ammonia	Thick, rigid mass	Partial, precipitate	15	100	0.5	0	0
Oxidized petroleum, alkalized with ammonia	Same	Partial	12	100	0	0.1	0.2
Nitrated SFA, alkalized with ammonia	"	"	31	100	0	0	0.5
Nitrated alkylphenol, alkalized with ammonia	Brown liquid, 50	Complete	10	100	3	0.1	0.2

¹ Recalculated to active component.

At the present time, corrosion inhibitor-additives to fuels consisting of mixtures of various compounds are widespread [6,8,9,13,14].

Several corrosion inhibitor compositions were tested in various ratios, for the purpose of study of their compatibility and effectiveness.

It was determined that the combination of the majority of the oil-soluble corrosion inhibitors are more effective than each of the individual compounds in the mixture. Thus, a mixture of three substances containing sulfo groups, nitro groups and amino groups, exceed the sulfonates, nitro oil or amine corrosion inhibitors in protection effectiveness. Moreover, combinations of various substances make it possible to obtain an additive with increased solubility in fuel. For example, the average-molecular-weight petroleum sulfonates, having high solubilizing properties, can include micelles of substances which are partially soluble in fuel, forming completely soluble systems.

As a result of the work carried out in selection of compositions, two combined fuel additives were selected: KP-1 and KP-2. The KP additives are produced by mixing acid sulfo and nitro products. The combined additive production technology is simpler, and the quality is better than that of common additives. The KP additives are ash-free, dark brown in color, and they are mobile liquids, which are transparent in a thin layer. The additives are characterized by the following indices: viscosity at 100°C, 12-13 centistokes, bromphenol blue alkalinity, 6 mg KOH, acidity in mg KOH, 62 for KP-1 and 70 for KP-2, content of active substance as percent of additive, 55 for KP-1 and 65 for KP-2, solubility in fuel, complete.

After testing in smoky diesel fuel combustion gases, according to GOST 305-63, 250°C, 20 min, with 0.5% KP additive, based on active component, plates of steel 45 turned out to be sparkling and there was no corrosion. In testing in

- smoky gases after combustion of diesel fuel without additives, plates of steel 45 proved to be dark and they had 10 point corrosion.

In the chamber and in tests at the "fuel-water" interface, corrosion did not appear, even after 30 days testing, both on steel plates (steel 45, steel 3), and in plates of nonferrous metals: aluminum, copper, brass, duralumin, bronzes (the corrosion value on nonferrous metals was determined by loss of weight of the plates, with four-figure accuracy).

There are data that, in combustion of sulfur-containing diesel fuels, the greatest corrosion can be observed at low (100°C) and high (500°C and over) temperatures and that, under these conditions, in the case of combustion of uninhibited fuel, the entire surface of the plate was corroded, the plates became dark and corrosion spots appeared on them.

In burning fuel with KP additive, the plate surface remained clean and sparkling, just like before the test.

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