

MECHANISM OF ACTION OF RUBBER BY PRODUCTS FROM THERMAL OXIDATION OF HYDROTREATED FUELS

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It has been suggested [1] that the source of accelerated aging of rubbers used in fuel pumps of gas-turbine engines operating on hydrotreated fuels is the oxygen-containing products formed in the fuel upon oxidation.

It is well known that the process of hydrocarbon oxidation is accompanied by the formation of stable oxidation products (alcohols, carbonyl compounds, acids) and less stable products such as hydroperoxides or peroxides and free radicals.

The present work was aimed at studying the effects of these oxidation products on Grade IRP-1078 rubber, which is used in fuel pumps, and was also aimed at using this information to develop measures to improve the properties of fuels relative to mechanical rubber goods.

This study was carried out with the individual hydrocarbons cetane, cumene, and decalin, which are representative of the main hydrocarbon classes present in jet fuels; also used in this study were standard fuels differing in chemical composition. The two types of apparatus were a static unit for fuel oxidation (OTSU instrument) and a bubbling unit (BOT).

The OTSU instrument consists of an electrically heated thermostat with four metal bombs, each 450 cm³ in volume, in which glass beakers are placed, containing the test hydrocarbon or fuel (200 cm³ sample) and IRP-1078 rubber specimens, die cut in the form of a Type V blade (GOST 270-64).

The BOT unit consists of a 200-cm³ cylindrical glass reactor with a porous filter designed for bubbling in an oxidant (air).

The rubber specimens after exposure were tested for strength (GOST 270-64).

A study of the hydrocarbon oxidation kinetics in the BOT unit at 150°C showed that, when the rubber was present, oxidation of the hydrocarbons was suppressed, indicating transfer of antioxidants from the rubber to the hydrocarbons. These antioxidants (aldol- α -naphthylamine, Neozone D) are used in the rubber to prevent its aging in air.

In order to avoid the influence of the antioxidants on the processes of interaction of fuel oxidation products with the rubber, tests were run on samples of rubber from which the antioxidants had been extracted by treatment with cetane for 4 h at 150°C in the OTSU apparatus without any oxidant. A preliminary study was made of the kinetics of antioxidant extraction from the rubber by the various hydrocarbons and fuels. It was established that, under these conditions, the cetane completely removed both antioxidants from the rubber, without any deterioration of the rubber mechanical properties. Kinetic curves are shown in Fig. 1 for the extraction of the aldol- α -naphthylamine from the rubber by cetane, cumene, and decalin, these data having been obtained by photocalorimetric analysis.

The results obtained on the extraction of Neozone D from the rubber are presented in Table 1.

Complete "washout" of the antioxidants from the rubber by cetane when treated under these conditions was confirmed by the identical kinetic curves obtained for hydrocarbon oxidation in the presence or the treated rubber specimens or in the presence of rubbers that had been specially compounded without antioxidants.

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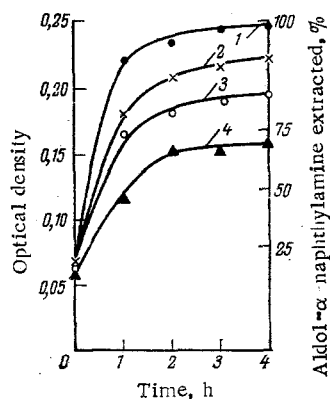


Fig. 1. Change in optical density of cetane, cumene, and decalin due to contact with rubber, in relation to time of treatment: 1) cetane, 150°C; 2) cumene, 150°C; 3) decalin, 150°C; 4) cetane, 20°C.

TABLE 1. Content of Neozone D in Rubber Specimens after Contact with Hydrocarbons at 120° and 150°C

Hydrocarbon (extractant)	Temperature, °C	Contact time, h	Presence of Neozone D in rubber
Cetane	120	1	Present
		2	"
		3	"
		4	Trace
	150	1	Present
		2	"
Cumene	150	1	Present
		2	"
		3	Trace
		4	Absent
Decalin	150	1	Present
		2	"
		3	Trace
		4	Absent

TABLE 2. Influence of Stable Oxidation Products on Rubber Properties

Expt. No.	Medium	Content of oxidation products in test fuel				Conditions of contacting with rubber	Strength of rubber	
		hydroperoxides, mmoles/l	acids, mmoles/liter	carbonyl compounds, mmoles/liter	alcohol, mmoles/liter		tensile strength, kgf/cm ²	elongation, %
1	Cetane, preoxidized	0,031	340	3,7	1,7	In absence of oxygen	113	150
2	Severely hydrotreated fuel, preoxidized	0,44	210	33	56	"	110	135
3	Cetane (original)	0	1,8	0,7	0	"	110	150
4	Severely hydrotreated fuel, original	1,0	1,8	0,7	0	"	116	120
5	Severely hydrotreated fuel, original	1,0	1,8	0,7	0	In presence of oxygen	26	30
6	Air	—	—	—	—	Atmospheric oxygen	112	150

TABLE 3. Change in Rubber Strength in Relation to Concentration of Hydroperoxides Decomposed to Radicals (temperature 150°C)

	Time of hydroperoxide decomp. time			
	0 min	20 min	40 min	60 min
Hydroperoxide concentration, mmoles/liter	44	0,94	0,31	0,22
Tensile strength, kgf/cm ²	124	30	20	—
Elongation, %	200	40	30	—

*Rubber becomes hard and readily fractured.

TABLE 4. Change in Strength of Antioxidant-Free Rubber Specimens in Relation to Contact Time with Hydrocarbons and Concentration of Hydroperoxides

Oxidation time, min	Cetane			Decalin			Cumene		
	Hydroperoxide concentration, mmoles/liter	tensile strength, kgf/cm ²	elongation, %	Hydroperoxide concentration, mmoles/liter	tensile strength, kgf/cm ²	elongation, %	Hydroperoxide concentration, mmoles/liter	tensile strength, kgf/cm ²	elongation, %
20	0,8	93	100	3,1	98	110	4	77	100
40	2,5	89	110	16	34	50	14	a*	a*
60	6,3	23	20	25	21	30	9	5,3	10

*Rubber specimen hardens and breaks immediately upon removal from reactor.

The extraction of antioxidants from rubber quite probably represents the first stage in aging of mechanical rubber goods under the conditions of fuel pump operation.

Results are presented in Table 2 from a study of the effects of stable oxidation products and atmospheric air on the strength of rubbers from which the antioxidants have been extracted; also listed in Table 2 are the conditions under which these experiments were conducted.

In experiments Nos. 1-2, the rubber was exposed to hydrocarbons and stable oxidation products, i.e., alcohols, carbonyl compounds, acids, and peroxy compounds (the concentration of the latter did not change during the course of the tests). In experiment No. 3, the rubber was exposed to the hydrocarbon alone, and in No. 4 to hydrocarbons and peroxy compounds (the latter were formed in the fuel during storage; no decomposition of these compounds was observed upon heating to 150°C). In experiment No. 5, oxidation took place, with the formation of stable oxidation products, unstable hydroperoxides, and free radicals [2].

In experiment No. 6, the rubber was oxidized with atmospheric oxygen. This experiment was performed to determine the effect of molecular oxygen.

Comparing the results of these experiments, we see that molecular oxygen, as well as stable molecular products of oxidation (including stable peroxy compounds) and the hydrocarbons themselves, is not aggressive toward rubber. A sharp deterioration of the rubber properties is observed under conditions of occurrence of the oxidative process, when relatively unstable hydroperoxides and free radicals are present in the fuels along with the other types of compounds just mentioned.

In order to determine the effect of hydroperoxides and free radicals on the rubber, the following experiments were performed.

Rubber specimens were tested in oxidized T-6 fuel [hydrotreated jet fuel] with (0.1% by weight) and without Ionol [2,6-di-tert-butyl-4-methylphenol], which is an acceptor of active radicals. The tests were performed in the OTSU apparatus with a 4-h exposure period at 140°C, without air. During the tests, the hydroperoxide concentration decreased to 0.2 mmole/liter as a result of decomposition to form free radicals. When the Ionol was present, the rubber did not change in mechanical properties; without the Ionol, the rubber completely lost its elasticity.

TABLE 5. Change in Strength of Rubber after Testing in T-6 Fuel (OTSU apparatus, 4 h, 150°C)

Fuel	Initial hydroperoxide concentration, mmoles/liter	Ionol content, wt. %	Strength of rubber	
			tensile strength, kg/cm ²	elongation, %
T-6, freshly produced	0	0,003	80	120
T-6 after long-term storage	0,2	0	28	21
	0,2	0,003	43	60
	0,2	0,01	92	140

The deterioration in mechanical properties of the rubber is shown in Table 3 in relation to the change in concentration of cetane hydroperoxide through decomposition to free radicals, these data having been obtained in experiments that were analogous except for the absence of any free radical acceptor.

These studies have shown that hydroperoxides prior to decomposition apparently do not have any effect on the mechanical properties of rubbers. The deterioration in properties comes about through the action of free radicals.

It is well known [2] that hydroperoxides decompose to form RO[•] and OH[•] radicals, which typically have very short lifetimes. Reacting with hydrocarbon molecules, these radicals form alkyl radicals R[•], which have considerably longer lifetimes; hence, the rubber is subjected to the action of R[•] radicals under these particular conditions.

In the initial stage of fuel or hydrocarbon oxidation in the presence of rubber in a stream of oxidant (air), the rubber is subjected mainly to the action of RO₂[•] radicals, as the concentration of R[•] radicals under these conditions is several orders of magnitude lower and can be neglected for practical purposes [2].

Data are presented in Table 4 illustrating the change in rubber specimen strength in relation to time of contact with oxidized hydrocarbons and in relation to the concentration of hydroperoxides. These experiments were performed in the BOT unit at 150°C.

These results showed that, under these particular conditions, the rubbers lost strength rapidly. It could be determined visually that the rubber had hardened within 40 min, and within 1 h it had become brittle and fragile. Similar results were obtained in oxidation tests on hydrotreated and hydrogenated fuels.

These data provide evidence for the high activity of RO₂[•] radicals with respect to rubber.

As shown above, hydroperoxides and peroxides probably do not cause rubber aging unless they decompose to radicals. However, the presence of hydroperoxides and peroxides in fuels is still not permissible; in the first place, they do represent a source of aggressive radicals (beginning at a certain temperature that depends on the structure of the compound), and in the second place, they initiate the oxidation process through the action of the radicals formed by decomposition.

As an example, we studied the aging of rubber in cetane during oxidation at 140°C, with and without an oxidation initiator (dicumyl peroxide, 0.01% by weight). The experiments showed that the oxidation of the cetane is more severe and the aging of the rubber far faster when the oxidation initiator is present.

These studies have shown that, in order to improve the service properties of hydrotreated and hydrogenated fuels with respect to rubbers, antioxidants that are acceptors of active radicals must be added to the fuels. This doping with antioxidant must be performed at the refinery itself, in order to eliminate the possible accumulation of peroxy compounds in the fuels during storage and transport.

Data are presented in Table 5 to illustrate the change in rubber strength after testing in oxidized T-6 fuel with different contents of hydroperoxides and antioxidant (Ionol).

It will be noted from Table 5, that, in the freshly produced T-6 fuel, which did not contain any peroxy compounds, an Ionol concentration of 0.003% by weight was adequate to prevent rubber aging. In the T-6 fuel that had been placed in long-term storage, a large amount of peroxy compounds had been formed, so that the use of 0.003% Ionol was relatively ineffective; only when the Ionol concentration was increased to 0.01% was it possible to eliminate the aggressivity of the fuel with respect to the rubber.

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RAPID METHOD FOR DETERMINING STABILITY OF M-12B, M-14B, AND M-14V₂ MOTOR OILS AGAINST AGGREGATION

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Petroleum-based lubricating oils are semicolloidal solutions in which molecules, ion radicals, and complexes in various degrees of dispersity exist side by side. According to the laws of thermodynamics, such systems will tend to decrease in free energy spontaneously, by consolidation of the particles. This is prevented by stabilizing components that either occur naturally in the oil base stocks or are introduced in the form of additives. If the effectiveness of the stabilizers drops off for any reason, the system loses its stability. This will produce coalescence (coagulation) of the micelles of the additive components in fresh oils; in the case of used oils, it will also produce coagulation of the solid contaminants that had been stabilized by the additive. The common feature of these processes is the elimination or surmounting of a stabilizing barrier. The temperature has a major influence on the stability of additive oils against aggregation. If the dispersant is inadequate in thermal stability, the dispersant molecules will be decomposed upon heating and will lose their effectiveness. In this situation, the solid contaminant particles in oils operating in diesel engines will coagulate and, together with the additive, will form a spongy mass. If the coagulation temperature is higher than the temperature of the oil-cooled surfaces, there will be no disruption of the diesel operating regime. If the reverse is true, the mass formed through particle coagulation will begin to deposit on the heated surfaces, with an adverse effect on the conditions of heat transfer. The use of an oil with a low coagulation temperature in diesels with oil-cooled pistons often leads to burnout of the piston heads. This phenomenon has been observed repeatedly when using M-14B oil (specification TU 38-101-264-72) in 11D45 high-performance locomotive diesels [1].* The lower the coagulation temperature, the more rapidly and in greater volume will a resinous or tarry mass separate out on the oil-cooled surface. Hence, a knowledge of the coagulation temperature is extremely important, not only for engine operators in establishing rejection levels for oils, but also for engine builders in selecting oils for newly developed engines.

The influence of coagulation temperature on the quantity of deposits in the oil-filled hollows and passages in cooled pistons was tested experimentally in an IDM engine unit. In Fig. 1, the quantity of deposits formed on the oil-cooled piston head is shown as a function of the coagulation temperature of Group B oils from various suppliers (all other test parameters being kept constant). The temperature to which the piston was heated, as measured by fusible inserts, was 220-230°C in these experiments. Hence, the quantity of deposits should be minimal when the additive coagulation temperature is above 230-240°C, and this was indeed confirmed by the experimental data.

It was established that M-12B and M-14B oils containing 8% of the additive VNII NP-360 [Ba alkylphenolate and zinc bis(alkylphenyl)dithiophosphate] are the least stable. However, a breakdown of stability was also registered in the process of operation on certain batches of M-14V₂ oil (specification TU 38-101-421-73).

*No literature citations are given in the Russian original - Translator.

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