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REVIEWS

FUEL ADDITIVES: EVOLUTION AND USE IN 1996-2000

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In a continuation of the reviews in [1, 2], materials published in the last five years of the 20th century are examined. Journal publications, patents, reports, and other communications concerning the evolution and use of fuel additives are used as sources. The world patent situation in this area and the basic trends in recent years, especially those relating to our country, are examined.

Approximately 500 original patents on fuel additives are published each year in the world. The patenting dynamics by basic types* of additives from 1981 to 2000 is shown in Fig. 1. Detergent additives for automotive gasolines have stimulated the greatest interest of developers. Diesel fuel depressants are in second place and atmospheric resid depressants are in a lower position. However, the intensity of development of depressants is gradually decreasing.

The decreased interest in antioxidants and stabilizers should be noted. As for ignition modifiers (antiknock compounds and additives that increase the cetane number), the number of developments in this area has again begun

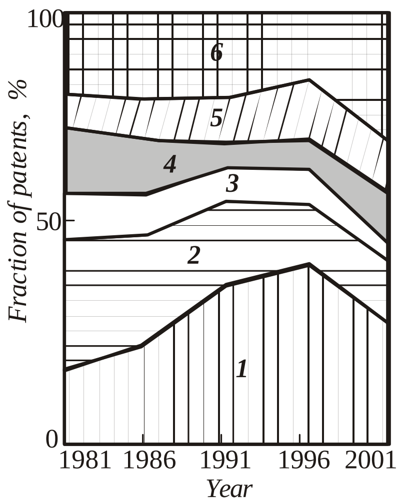

Fig. 1. Patenting of different types of fuel additives in 1981-2000: 1) detergents; 2) depressants and wax dispersants; 3) antioxidants, metal deactivators, stabilizers; 4) ignition modifiers; 5) combustion modifiers; 6) other.

*Additives are separated by types according to the classification in [3].

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TABLE 1

Type of additive	Total number of patents published in 1996-2000	
	national	with consideration of national and European patents
Detergents for automotive gasolines	93	129
Depressants and wax dispersants	48	71
Antiknock compounds	54	55
Ignition promoters	8	10
Antioxidants	2	2
Stabilizers of complex action	6	6
Biocides	1	1
Smoke suppressants and combustion catalysts	65	76
Detergents-scavengers for diesel fuels	16	17
Antiwear for low-sulfur diesel fuels	21	51
Antifoaming	9	14
Other	69	100
Total	392	532

to increase after a slight drop in 1991-1995. The causes are the active searches for alternative antiknock compounds in Russia, China, and some other countries, and the development of additives to increase the cetane number of diesel fuels in Europe and the US.

A great deal of attention has also been focused on combustion modifiers. Additives containing combustion catalysts – fuel-soluble metal compounds that improve fuel combustion, facilitate burning of carbon deposits and thus decrease the toxicity of engine exhaust gases – are characteristic of western countries. In Russia, much attention has been focused on smoke-suppressant additives that reduce the formation of black smoke. Additives of other types which have been the subject of one or more patents during the five-year period are classified as "others." Patenting of antiwear additives for low-sulfur diesel fuels has increased rapidly, among others.

More detailed information on the structure of patenting of additives in 1996-2000 is given in Table 1. However, automotive gasoline additives of the oxygenate type, which we will consider as fuel components, and commercial forms, which are dilute additives retailed as automotive products, are not considered in these statistics. Patents of new methods of producing existing additives and patent analogs issued for the same additive in different countries are not taken into consideration.

The patents reported in Table 1 should not be considered absolutely exhaustive since the patents on some inventions have not been published or are published after a long delay (up to five years). It is also necessary to remember that some companies prefer not to patent the most promising inventions but instead to keep them secret as know-how.

The data in Fig. 2 characterize the participation of different countries in patenting of fuel additives. As previously, the US is the leading country in this area: its share in the period examined was approximately 28%. It should be noted that it was previously much higher, approaching 50%. The decrease was the result of an increase in the activity of several countries, Russia and China in particular, and an increase in international patents.

Russia has been in second place in patenting of fuel additives after the US in recent years, displacing Japan and Europe. The share of patents published by Russia and inventor's certificates in world patenting did not exceed 2-3% in previous periods, but increased to 20% in the last five years. In our opinion, this rapid increase is due to the economic advantage of patenting in Russia. The activity of domestic developers has increased for this reason.

The priorities of different countries in patenting the individual types of additives can be evaluated with the data in Tables 2 and 3. For Russia, alternative antiknock compounds are such a priority due to the insufficient

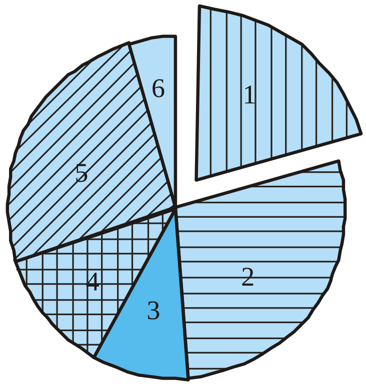

Fig. 2. Structure of patents by country and region in 1996-2000: 1) Russia; 2) USA; 3) Japan; 4) Europe; 5) other countries; 6) international and European patents.

domestic capacities for production of high-octane components of automotive gasolines – catalytic, alkylate, isomerizate cuts. Great attention is being focused on alternative antiknock compounds in some other countries, primarily China, as well.

Detergent additives to automotive gasolines are being most intensively developed in the USA due to both this country's approach to the use of detergent additives (obligatory under the Clean Air Act) and the amount of gasoline consumed. In 1990, consumption was 365 in the USA, 125 in Western Europe, and 23.5 million tons of gasoline in Russia [4].

In Japan, attention is divided almost equally between detergents and depressants. The proportion of heavy fuels has traditionally been high in this country's fuel balance. However, the interest in detergents has been gradually increasing in the last 20 years, while the interest in depressants has decreased.

CHARACTERISTICS OF ADDITIVES

Detergent additives are still fundamental with respect to the volume used and number of commercial brands. Additives that wash deposits off the valves in fuel-injection engines are primarily used abroad. As in previous years, the fundamental brands are represented by polyether amines and polybutene amines.

There have been no important new technical solutions in this area and such solutions can hardly be anticipated since the interest of developers is gradually switching to additives that wash the primary combustion space. Valve cleaners are necessary for engines with distributed injection of gasoline into the valves. Such engines are now the most common ones in the US and Europe. However, engines with direct injection of gasoline into the cylinders are more economical. Their expansion was held back by a number of technical difficulties which have now been overcome.

It is suggested in [5] that engines of this design are the most promising. Additives that wash the primary combustion space more than the valves are required for their operation. Such additives are surfactant (SF) compositions which are sometimes combined with carbon modifiers (alcohols, esters) and combustion catalysts (iron, copper, manganese, rare-earth element compounds). Most primary combustion space cleaners can be used in both gasoline and in diesel engines [6].

The method developed at Shanghai University merits attention [7], although it does not formally pertain to use of additives. Here ~100 cm^3/cm^3 of carbon dioxide is dissolved in diesel fuel. This partially models recirculation of exhaust gases: due to the high heat capacity of carbon dioxide, the temperature in the primary combustion space and emissions of nitrogen oxides decrease. In addition, carburetion is improved due to explosive evaporation of carbon dioxide during expansion.

There is also a chemical effect: soot is directly oxidized by carbon dioxide; in addition, $O\cdot$ and $OH\cdot$ radicals are generated and also cause gasification of soot. In contrast to standard recirculation of exhaust gases, the danger of increased engine wear and emission of soot with full loads are decreased.

Antiknock compounds. Although alkyllead antiknock compounds were patented in the period examined [8, 9], we will only consider the so-called alternative antiknock compounds containing no lead compounds.

TABLE 2

Country, region	Share (%) in patenting* of additives in 1996-2000				
	detergents	depressants	antiknock compounds	combustion modifiers	total in all patents
Russia	5.3	21.4	70.4	41.6	20
USA	61.4	14.2	11.1	22.2	28
Japan	14.0	32.2	0.0	5.6	13
Europe	15.8	21.5	3.7	25.0	19
Other	3.5	10.7	14.8	5.6	21
Total	100.0	100.0	100.0	100.0	100

Note. *Without consideration of international patents.

TABLE 3

Additives	Share (%) in patenting* in 1996-2000 by countries and regions				
	Russia	USA	Japan	Europe	other
Detergent	5.7	47.9	36.4	25.0	13.3
Depressant	10.3	5.5	40.9	16.7	20.0
Antiknock	35.8	4.1	0.0	2.8	26.7
Combustion modifiers	28.3	10.9	9.1	25.0	13.3
Other	18.9	31.5	13.6	30.5	26.7
Total	100.0	100.0	100.0	100.0	100.0

Note. *Without consideration of international patents.

There are three fundamental alternative directions: aromatic amines, ferrocene and its derivatives, and manganese carbonyl compounds. New additives are also being actively created in Russia in all of these directions.

Of the aromatic amines, N-methylaniline, which produces the highest increase in the octane number with the least effect on gum formation is almost exclusively used. With respect to the antiknock properties, these compounds are in decreasing order as follows: aromatic > heterocyclic > aliphatic > cycloaliphatic [10]. Data on the octane numbers of a mixture of aromatic amines are published in [11] (Table 4). Some compounds are more effective than N-methylaniline, but a drawback is increased gum formation in the primary combustion space and fuel system parts. On the contrary, in addition to N-methylaniline, xylidenes have also been approved for use in Russia [12], but only in order to utilize the reserves in Army warehouses [13].

Of the ferrocene compounds in antiknock compositions, alkylferrocenes [14] and dimethylferrocenylcarbinol have been most widely used. The latter is used in Russia under the name FK-4 in production of automotive gasolines and as a component of Angarad-2401 smoke-suppressant additive [15]. A number of additives containing unsubstituted ferrocene has been patented in China [16].

Iron compounds were widely used as antiknock compounds in Russia in 1960-1970, but they were then considered unpromising primarily due to the high formation of deposits on spark plugs which perturbed their operation and led to accelerated wear. It has not been possible to find effective iron evacuators similar to lead evacuators. Modern developers were again faced with the same problem, but they established the maximum acceptable concentrations (38 mg Fe/liter) at which high fouling is not observed [17].

Manganese compounds have been more common than iron compounds. Methylcyclopentadienylmanganese tricarbonyl (MCMT) is almost exclusively used in practice. It was approved for use as the additive Hitec-2000 (Ethyl Corp., USA) in Russia in 1995. The maximum concentration in fuel that prevents increased wear and fouling has been established: 50 mg Mn/liter.

TABLE 4

Aromatic amines	Octane number of mixture by	
	MON	RON
Aniline	290	310
p-Toluidine	305	340
p-Ethylaniline	300	320
p-*tert*-Butylaniline	250	280
3,4-Xylidene	320	370
3,5-Xylidene	210	340
N-methylaniline	250	280
N,N-dimethylaniline	84	95

The concentrations of alternative antiknock compounds in gasolines are limited for different reasons. For this reason, the possible increase in the octane number in use of some type of additive is also limited (Table 5).

A large number of developments concern composite antiknock compounds containing amines, iron and manganese compounds, and oxygenates in different combinations. This allows summing the antiknock effect of the additives and obtaining a synergistic effect in some cases. The great experience in Russia allows drawing a conclusion concerning the functional compatibility of additives (Table 6).

It is advantageous to use antiknock compounds even in the case of antagonism, although the effect obtained is smaller than the overall effect. It is senseless to list all composite antiknock compounds, since the number of possible variants is very large and there are also many approaches to creation of the compounds. Another type of composite includes antiknock compounds and detergents, for example: MCMT, N-methylaniline, and Avtomag [18]; ferrocene compounds, aromatic amines, and Avtomag [19].

Smoke-suppressant additives, as noted above, are not of interest for Western Europe, the USA, and Japan. Attention is paid to them in Russia, as previously. Smoke-suppressant additives reduce emissions of black smoke (actually soot) with the exhaust gases from diesel engines.

Black smoke is formed in engine overloading and augmentation and in fuel system malfunctions. Some metal compounds cause soot to burn, primarily barium, manganese, and calcium compounds. Barium compounds are most effective. They are also proposed as smoke-suppressant additives.

Lubrizol (USA) has dominated the market for these additives for a long time. The domestic additive IkhP-706 was created in the USSR in the 1970s, and EKO-1 and EFAP-B additives were developed in Russia in the period investigated. The last one has been approved for use. It was patented [20] by LUKOIL–Volgogradneftepererabotka Ltd., where it is also manufactured in a small volume primarily to satisfy the company's needs.

Barium smoke suppressants are virtually not used abroad, primarily due to prohibition of ash components, the cause of emission of solid particles with the exhaust gases, in light fuels. In addition, organization of the operating process does not allow black smoke in diesel engines manufactured by the leading foreign companies. However, as previously, Lubrizol offers its own additives to countries with less strict requirements for exhaust gases. One such additive, Lubrizol-8288, has been approved for use in Russia [21].

Combustion catalysts. This comparatively new type of additive is drawing the attention of developers in all countries. The principle of their action consists of a catalytic effect on combustion of hydrocarbons. They contain manganese, iron, cerium, and other catalytically active metal compounds. The working concentrations of combustion catalysts are very low and are set so that the concentration of metal in the fuel is no greater than thousandths of a percent. The additives can also contain SF, carbon deposit modifiers, and other additives.

Such additives are available on the retail market abroad and are intended for user discretion. Two additives from the Academy of Applied Research Closed Joint-Stock Company which allow manufacturing environmentally improved automotive gasolines and diesel fuels have been approved for use in Russia. When combustion catalysts

TABLE 5

Additives	Limitation of concentration in gasoline	Maximum increase in octane number	Cause of limitation
Aromatic amines	1 – 1.3%	6	Gumming of engine and fuel system parts
Iron-containing	38 mg Fe/liter	3 – 4	Increased wear and fouling on spark plugs and in primary combustion space
Manganese-containing	50 mg Mn/liter	5 – 6	the same

TABLE 6

Alternative antiknock compound	Lead	Iron	Manganese	Amines	Oxygenators
Lead		–	–	+	+
Iron	–		–	+	–
Manganese	–	–		+	0
Amines	+	+	+		+
Oxygenators	+	–	0	+	

Notes. + = synergism; – = antagonism; 0 = simple summation.

are used, emission of products of incomplete fuel combustion and solid particles, primarily soot, is reduced by 30-50%.

The mechanism of action of combustion catalysts in fuels has been insufficiently investigated. In studying ferrocene additives, it was found in particular that ferrocene forms condensation sites (hypothetically iron oxides) before carbon particles are formed in the combustion zone. The carbon particles are condensed on them and are totally burned in the following stages of the process [22].

There are more original technical solutions for use of combustion catalysts. For example [23], the inner surfaces of the fuel tank and pipelines can be coated with a catalytic composition containing up to 40% Sb, up to 20% Ba, Cd, Ca, Pb, Ni, up to 10% Ag, Pt, Ru, Ag, and up to 80% Sn. In another case, the precious metal compound is added to the gasoline so that the metal precipitates on the walls of the vessels and has a catalytic effect on secondary combustion of exhaust gases [24] or restores catalytic neutralizer activity [25].

Ignition promoters. The content of highly aromatized cuts obtained in destructive refining of petroleum residues – catalytic gasoils – is increased in diesel fuels with more exhaustive refining of the crude oil. These cuts have a very low cetane number, so that ignition promoters are added to the fuels that contain them. This problem is becoming very acute abroad.

With respect to the feedstock balance, most Russian refineries have a small reserve with respect to the octane number, but it will be exhausted in the future not only due to more exhaustive refining of crude oil but also due to bringing the cetane number of domestic diesel fuels to the level of foreign fuels. This is required for supplying fuels for export and will become necessary when the new Russian standard becomes active.

Domestic fuels for high-speed diesels must now have a minimum cetane number of 45 and according to the World-Wide Fuel Charter requirement, from 48 to 55 as a function of the category of fuel [26]. Of the basic types of ignition promoters, preference has traditionally been given to alkyl nitrates, but azo compounds [27] and alkyl peroxides [28] have also been proposed.

Antiwear additives for automotive gasolines. In going to unleaded gasolines, the problem of wear of exhaust valves made of soft steels arose. In designing these valves, it was assumed that lead oxides and sulfides, which have an antiwear effect, would be deposited on the surface of the seats when lead compounds were present. After use of tetraethyllead (TEL) was prohibited, wear of valve seats with less than 0.05 g/liter of lead in the gasoline can attain

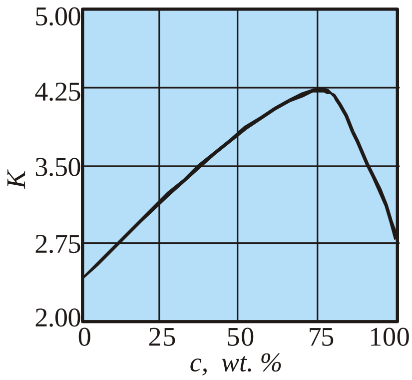

Fig. 3. Effect of the concentration *c* of barium alkylphenolate combined with composite of ethylene and vinyl acetate copolymer on diesel fuel filtration coefficient *K*. Total concentration of composite in fuel: 0.15 wt. %.

a critical level. For an average automobile speed of 100 km/h [29], a wear rate equal to 1 mm/h is assumed to be critical.

Two palliative solutions have been used for some time. The first consisted of using low-lead gasolines with a 0.05-0.075 mg/liter lead content and the second consisted of alternate filling with unleaded and leaded gasoline. In the second case, an aftereffect was used: the protective film of lead compounds on the valve surface persisted for 10-20,000 km after the engine was switched to unleaded gasoline.

However, in order to totally prohibit lead, it is necessary to use special antiwear additives. Phosphorus-containing compounds – scavenger components of ethylating liquids which not only prevent formation of carbon on spark plugs but also reduce valve seat wear – were initially such additives. These additives were dropped with the advent of catalytic neutralizers, since phosphorus is a poison for platinum and palladium catalysts.

Of the modern additives, alkali metal compounds have become widespread. For example, Shell offers an additive based on a potassium compound and its working concentration in gasoline (in terms of potassium) is approximately 8 ppm. With high concentrations, bedding of the exhaust valve and corrosion of turbines in the turbo supercharger system are possible.

Antiwear additives for diesel fuels. Diesel fuels with a low sulfur content are characterized by poor antiwear properties. It is believed that when the sulfur content in the fuel is less than 0.05%, special antiwear additives should be used. This problem is becoming especially acute in industrially developed countries and has already been clearly identified in Russia.

Many refineries are producing fuels with a low sulfur content both for export and for domestic consumption. The amount of these fuels is still small, but it will rapidly increase. The proportion of domestic fuels with a sulfur content below 0.05 and 0.1% in 1990, 1995, and 2000 was respectively 0.2, 3.8, and 12% of total fuel production [30].

In principle, a sufficient antiwear effect can be obtained by adding naphthenic acids, called additive K, to the fuel; they are highly recommended in hydrogenated jet fuels. However, in diesel engines the fuel is in contact with the oil and small amounts enter the crankcase. For this reason, there is an additional requirement for additives – they must not have a negative effect on the lubricating oil.

Acids do not satisfy this requirement since they break down some additives contained in motor oil and deposits form in the fuel and oil system, creating the hazard of corrosion of cylinder–piston group parts.

The most common additives of this type contain carboxylic acid derivatives: esters [31], amides [32], products of transesterification of vegetable oils and animal fats with alcohols or phenols [33], hydrocarbons with several polar functional groups, amino groups or hydroxyls, for example [34], etc. On the contrary, some patents provide for the use of different variants of carboxylic acids [35].

Oxygenates. The volume of oxygenates used in automotive gasolines is increasing from year to year. They not only allow increasing the octane number of gasolines but also increasing the feedstock resources due to

TABLE 7

Type of additive solution in fuel		Observed effect of fuel additives
first	second	
Real	Real	Compatibility
Real	Colloidal	Compatibility or potentiation of the effect of one or both additives
Colloidal	Colloidal	Compatibility or antagonism manifested as physical or functional incompatibility

TABLE 8

Type of additive	Proportion (%) of patents in total number in 1990-1999	
	abroad	in Russia
Detergents of all types	44	5
Depressants	14	9
Antioxidants and stabilizers	6	0
Antiknock compounds	4	46
Ignition promoters	2	0
Combustion modifiers	15	25
Other	15	15

petrochemical products. In addition, there are technologies [36] in which the olefins contained in many gasolines are alkylated with methanol, and this reduces the olefin content in the commercial gasoline.

It is hypothesized that oxygenates decrease the toxicity of automobile exhaust gases. For this reason, the US Clean Air Law passed in 1990 provided that: reformulated gasoline must contain an amount of oxygenates at which the concentration of oxygen in the gasoline will be a minimum of 2%. Lower alcohols and ethers, primarily MTBE – methyl-*tert*-butyl ether, are used as oxygenates. It provides the widest feedstock base – isobutylene and methanol.

However, in the USA, the attitude toward MTBE has changed strongly in the last five years. It was noted that it seeps out of underground tanks and contaminates ground waters due to its good solubility in water: 4.8% at 20°C. In California, legislation prohibits positioning pipelines and filling stations operating with MTBE closer than 300 m from sources of drinking water [37].

In 1999, the US Environmental Protection Agency eliminated the requirement of a mandatory 2% oxygen content in reformulated gasoline [38]. Beginning in 2002, MTBE will be prohibited in production of gasoline in the state of California. Ethanol is the most acceptable alternative. Different variants of its use have been patented in many countries, including Russia.

Depressants and wax dispersants. In the period examined, the principles for improving the low-temperature properties of diesel fuels were finally defined. It was shown that traditional depressants (polyacrylates and copolymers of olefins and vinyl acetate) do not prevent separation during cold storage by reducing the solid point of the fuels. As a result, the fuel separates into two layers: an upper, clear layer and a lower, cloudy layer rich in waxes. Both layers are mobile, but when fuel is taken off from the lower layer, the engine misses.

Special additives – wax dispersants or precipitators – solve the problem. Their effect consists of formation of very small wax crystals with high sedimentation stability. When a depressant is added, the crystal size decreases from 60 to 10 mm and when wax dispersants are added, it decreases from 60 to 1 mm [39]. X-ray examination showed that the shape of the crystals also changes – from rhombic (with traditional depressants) to hexagonal (on addition of dispersants).

The idea of creating an electric charge on the surface of nascent crystals which would push the crystals away from each other and not allow them to grow into large formations was implemented in developing wax dispersants.

TABLE 9

Type of additive	Use in fuels	
	abroad (in industrially developed countries)	in Russia
Antiknock compounds		
based on TEL	With rare exceptions, prohibited	Rapidly decreasing
alternative	Virtually not used (iron and manganese compounds are prohibited in many countries)	Officially permitted in extreme cases, but developments in this area are proceeding very actively
Detergents for gasolines	Use mandatory, effect in both carburetor and diesel engines	Occasionally used, obsolete, but effective in carburetor engines
Depressants	Used if necessary	High demand is satisfied by imports. Domestic production volume insignificant
Smoke-suppressants	Not used, but manufactured for marketing in other countries	Domestic additives, used occasionally

For this reason, the structure of the molecules of wax dispersants differs from the structure of depressant molecules. They are acid amides, polymers modified with amino groups, etc. [40].

Additives of this type are not used independently but only in compositions with depressants. Additives that combine both of these useful properties have been developed. Wax dispersants are especially important in countries with long winters. In Russia, for example, the use of depressant and wax dispersant compositions is strongly recommended.

Other additives. Of these additives, we mention antifoaming agents; the number of patents for these agents is increasing. This is because antifoaming properties are standardized by the World-Wide Fuel Charter requirements for category 3 fuels with improved environmental and operating properties [26]. Almost all of these additives are made from siloxanes modified with different substituents [41]. Use of quaternary ammonium salts containing hydroxyethylated fragments bound with a nitrogen atom is also proposed [21].

Antifoaming additives are sometimes incorporated in multifunctional compositions containing detergent, lubricating, and other agents [42]. We also note the additives that reduce losses in evaporation of gasoline [43]. The principle of their effect consists of formation of a strong adsorption film on the surface of the fuel which impedes migration of hydrocarbon molecules into the gas phase. They contain compounds with elevated surface activity and relatively high molecular weight as the active component, polysiloxanes, quaternary ammonium salts, etc., for example. Additives of this type were also developed previously, but have not yet been used, although in principle they should be of both economic and environmental interest.

COMPATIBILITY OF ADDITIVES IN FUELS

The question of the compatibility of additives was not raised until recently, since the same fuel sample very rarely contained more than one additive. The situation has changed in recent years.

First, the assortment of additives has increased. For example, diesel fuel can simultaneously contain smoke-suppressant and depressant additives, automotive gasoline can contain an antiknock compound, antioxidant, detergent additives, etc. Second, due to wide retail sale, the use of fuel additives has become uncontrollable. For this reason, specialists have observed cases of poor balancing of fuel additives.

To prevent this, refining of automotive gasolines with no additives at refineries and introducing them to the consumer have been proposed, in [44], for example. However, this approach is not always applicable. There are additives that must or can only be added at the refinery. These include antioxidants, antiknock compounds, ignition promoters, depressants, etc.

There is little work being done on the compatibility of fuel additives, although such research is necessary [45]. It was found that both synergism and antagonism can be observed in mixtures of additives. In addition, physical incompatibility is possible, manifested by a change in the colloid chemical state of the additives in the

TABLE 10

Type of additive	Function	Number of additives approved for use in automotive gasolines and diesel fuels		
		domestic	imported	total
Antiknock compounds	Increase octane number of automotive gasolines	14	1	15
Ignition promoters	Increase cetane number of diesel fuels	3	2	5
Antioxidants	Increase oxidative stability of gasolines during storage	5	0	5
Complex stabilizers	Increase chemical stability of diesel fuels during storage	1	0	1
Biocides	Give fuels resistance to biological contamination	1	0	1
Depressants and wax dispersants	Improve low-temperature properties of diesel fuels	5	12	17
Deicers	Prevent icing of choke valve	1	0	1
Smoke suppressants	Reduce diesel engine exhaust gas smoke content	4	1	5
Combustion catalysts	Improve combustion of automotive gasolines and diesel fuels	2	0	2
Detergents	Maintain optimum engine operation by decreasing formation of carbon and deposits	3	4	7
Antiwear additives	Increase operating life of fuel system on low-sulfur diesel fuel	0	3	3
Antiscuff additives	Accelerate running-in of engines during manufacture and running in	1	0	1
Dyes	Marking fuels for different purposes	3	1	4
Total		43	24	67

Note. A detailed list of additives approved for use in Russia as of 01.01.2000 is given in [13].

fuel. An example of physical incompatibility is described in [46], where thickening with subsequent separation of the fuel was observed when barium or calcium alkylphenolates and polybutene amine detergents were mixed.

There are also more complicated cases where the solution does not change externally when additives are mixed, but some of its properties, determined experimentally, worsen. As an example, the change in the filterability coefficient of diesel fuel containing a mixture of barium alkyl phenolate (EFAP-B additive) and a depressant based on a copolymer of ethylene with vinyl acetate (Keroflux-5486) in different ratios is shown in Fig. 3.

This coefficient increases sharply with a certain ratio of additives, obviously due to intermolecular interactions that result in the formation of complex micelles of the additives. Because of colloid chemical interactions, there can also be loss of the functional effectiveness of the additives. A case of antagonism between depressants and wax dispersants due to competition for the surface of the growing wax crystal is described in [47].

The observed cases of compatibility of additives are reported in Table 7 with consideration of the type of additive solution in the fuel [46]. This table will undoubtedly be corrected as new data are published.

CHARACTERISTICS OF PATENTING AND USE

Comparative data on the structure of patenting of fuel additives in Russia and abroad are reported in Table 8. As noted previously, abnormally high interest in alterative lead-free antiknock compounds is characteristic of our country. They to some degree compensate for the insufficient capacities for development of high-octane gasoline components. In addition, they are very advantageous for use by small manufacturers of gasolines based on gas condensate feedstock or commercial low-octane gasolines.

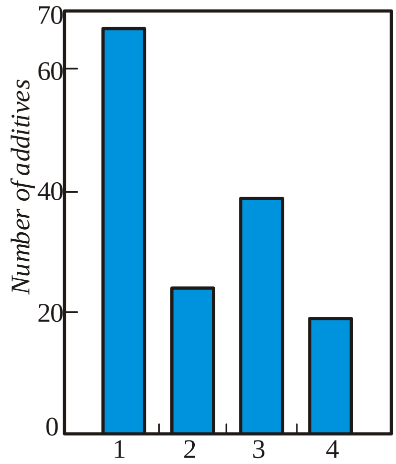

Fig. 4. Change in the number of fuel additives approved for use in Russia: 1) total on 01.01.2001; 2) including imported additives on 01.01.2001; 3) total for 1996-2000; 4) including imported additives for 1996-2000.

Additives of this type are either not used or are considered unpromising abroad. The use of ash fuel additives is prohibited by the US Clean Air Act and the World-Wide Fuel Charter [36]. The use of these additives in Russia is considered temporary. Gosstandart is issuing a permit for production and use of automotive gasolines with alternative antiknock compounds only in cases where rapid conversion to production and use of unleaded gasolines by another method is impossible.

Some features of the structure of use of additives in Russia are given in Table 9. It also gives some features in organization of use of additives. With the increase in technical crops, the domestic consumer is increasingly frequently using fuel additives. However, the retail sales volume is not high enough for manufacture of additives to be profitable. For this reason, the developers are attempting to guarantee marketing of their own additives and to organize production of fuels with additives at the refinery or in large fuel companies.

As examples, we mention NORSI OJSC, where production of the automotive gasolines NORSI A-76 and NORSI AI-80 with Avtomag detergent additive was organized in 1995 [48] and Petersburg Fuel Company, which has been producing and implementing Evro-brand gasolines and diesel fuels with 0011 and 0010 combustion catalysts since 1999 [49]. However, due to the lack of commercial economic interest, this is only possible in cases of legislative subsidy of the developers by regional authorities.

In conclusion, the statistics on permits for use of fuel additives in Russia as of 01.01.2001 are reported in Table 10. These are actually permits for use of fuel with additives, since permission to use the additives themselves is not provided for by the procedure. Since the same additive can be incorporated in different fuels and approved several times, in compiling the table, only the first approval, which can be considered the precedent, is included. Lead antiknock compounds, oxygen-containing additives, and products in the from of dilute additives were not considered in the statistics.

Most fuel additives in Russia, especially imported additives, were approved for use in the period examined (Fig. 4).

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