III. INTRODUCTION OF ECOLOGICAL CONSIDERATIONS INTO POWER ENGINEERING AND TRANSPORT

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Problems of the development of catalytic after-burners for the exhaust gases from automobiles and of alternative ecologically clean fuels

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The exhaust gases from internal combustion engines are the principal source of harmful pollutants in the atmosphere. Unfortunately, our Press has devoted little attention to this factor. The main bulk of publications objecting to the pollution of the atmosphere refer to the chemical industry and electric power stations. However, in reality the pollution of the atmosphere by automobiles is incomparable in terms of scale to the harmful effects of the chemical industry. In the chemical industry, pollution is more local and can be more readily detected by smell and colour than the automobile exhausts and for this reason is more likely to attract the attention of journalists.

The approximate composition of the spent gases from petrol engines is presented in Table 1. The composition of the gases naturally varies as a function of the type of engine and, in particular, the nature of the fuel. After catalytic cracking, petrol contains more paraffins and, after reforming it contains more aromatic compounds, etc. Most of the gases listed in Table 1 have no colour or smell.

According to an estimate,[1] in the USA there are 5.5 times more motor cars (110 million) than in the USSR (20 million). However, as a result of measures taken for the strict control of exhaust gases each automobile in the USA emits at least four times less harmful substances than in the USSR. The damage to human health in the USSR due to the pollution of the atmosphere caused by the exhaust gases from engines is estimated to cost 60 million roubles annually. It has been suggested that the overall scale of pollution of the atmosphere in 1990 will amount to 242 million tonnes, including 172 million tonnes due to motor cars. The exhaust gases from internal combustion engines are responsible for more than 70% of diseases among children. The incident of lung cancer and also the number of spontaneous miscarriages have increased. It is believed[1] that 68% of all the human diseases are induced by breathing poisoned air.

The interaction of nitrogen oxides NO_x with hydrocarbons under the influence of solar radiation induces the appearance of the so-called photochemical smog. Thus the exhaust gases from automobiles are particularly harmful in poorly ventiliated cities with a large amount of solar radiation such as Log Angeles, Alma-Ata, and Tbilisi. We emphasise yet again that smog is caused not so much by chemical or power industry as by motor cars.

I. Norms for the emission of toxic products

The principal methods for reducing the toxicity of autombile exhaust gases involve the improvement of engine design, the introduction of electronic devices for regulating the composition of gases, the improvement of the composition of fuel, and catalytic purification. The first studies on catalytic purification date back to the 1920s and systematic studies in this field were initiated in 1949 by E Houdry (USA).[2] However, the widescale incorporation of the results of these studies did not begin until the end of the 1970s after the U.S. government introduced controls for the emission of toxic substances and reduced the permitted norm (limit) for the latter.[2] Since then the norms for the emission of toxic substances have been continuously made more strict (Table 2).

The reason for this process has been the sharp impairment of the state of the atmosphere in cities with heavy motor traffic. The adoption of clean air laws and the stage by stage increase in the rigour of standards have led to serious steps being taken in the USA as regards the problem of the purification of motor car exhaust gases. In the course of an approximately 20 year period of observations, the level of emitted incomplete combustion products from newly produced motor cars has been reduced by a factor of ~ 10 and the level of nitrogen oxides has been reduced by a factor of 3–4.

Even more strict standards as regards nitrogen oxides have been adopted in Japan (Table 2). In Western Europe the 1988 norm is less rigorous but since that year newly produced automobiles in Europe began to be fitted with catalytic after-burners. There has been a corresponding diminution in the use of ethylated petrol and in 1990–1991 it should cease altogether. The norms for emitted gases in Western Europe gradually approach the American and Japanese ones. Application of norms to emissions has also been introduced in the USSR (Table 3).

It is essential to note that, owing to the complexity of the procedure for the determination of the exhaust gases (special equipment, driving cycles, etc.), the certification of a given model as regards toxicity and the issue of a special certificate guaranteeing that the automobile meets the specified ecological parameters at least

in the course of a guaranteed distance (80–160 km) have come to be generally adopted. Since the renewal of car fleets and models in Western markets takes on average 3–5 years, this specifiction of norms ensures the maintenance and in many cases the improvement of the ecological situation.

Table 1. Spent gases from petrol engines.

Components	c_{max}, vol.%	Toxicity
N_2	74–77	Non-toxic
H_2O	3.0–5.5	»
O_2	0.2–5.0	»
CO_2	0.5–12	»
CO	0.2–5.0	Toxic
NO_x	0–0.8	»
SO_2	0.02–0.1	»
Paraffins	0–1.2	»
Olefins	0–1.6	»
Aromatic compounds	0–0.4	»
Soot	0–0.4 *	»
Benzopyrene	up to 20*	Carcinogenic

* The concentration is expressed in g m^{-3}.

Table 2. The norms for the emission of toxic products in the USA, Japan, and Western Europe.

Country	year	Norm, g km^{-1}		
		hydrocarbons	CO	NO_x
USA*	up to 1975	6.2	52	3.4
	1975	0.93	9	1.9
	1980	0.25	4.3	1.2
	1985	0.23	2.1	0.62
Japan	1988	0.25	2.1	0.25
Western Europe	1988	0.86	6.17	1.63

* In 1990, George Bush signed the law concerning the further increase in the strictness of emission norms (including that for CH_2O).

One should also note the well tried procedure for the introduction of standards in the West, the combined approach to their application, and also the provision for legal and economic sanctions as regards the quality of fuels and oils, the system of financial incentives for the low toxicity of exhausts, etc.

The adoption in the USSR of sufficiently strict standards has unfortunately not led to a significant improvement of the atmosphere, as regards risks to health, in large cities for a number of reasons. In the first place, one should note the considerable gap between the quality of the exhaust from an automobile leaving the conveyer belt and an autombile in normal use — the extremely low quality of technical servicing and the long operating life lead to a toxicity several times greater than the specified parameters. The norms are simply not fulfilled. There exist considerable reserves also in the design and in the technology of the manufacture of the engine and of the means of transportation — random tests have shown that even on delivery a considerable percentage of Soviet automobiles do not meet the requirements of the standards.

Table 3. The norms for the emission of toxic products in the USSR.

Year of introduction	Weight category of automobiles	Norms, g m^{-1}		
		hydrocarbons	CO	NO_x
Actual standard OST 37.001.054–86	1250 kg	5.06	14.8	–
	1450 kg	5.43	16.8	–
For engines with catalytic converters				
1991	h=1.4–2.0 litres	1.97	7.4	–
1988	h > 2.0 litres	1.97	7.4	–
1990	h > 2.0 litres	1.63	6.17	0.86
For engines without catalytic converters				
1991	h=1.4–2.0 litres	3.7	11.1	1.48
1990	h > 2.0 litres	4.19	11.1	1.48

Note. h = volume of cylinders.

Another cause is the structure of the standards in the USSR, which have separate norms for automobiles without converters and for automobiles with converters [the latter are close to Western European norms]. However, when there are two norms, nobody tries to satisfy the stricter one. In view of the fairly liberal interpretation of standards, it is difficult to expect a serious effort by industry and operating organisations to achieve a radical decrease in the toxicity of spent gases.

Finally one should emphasise that extremely strict norms as regards toxicity can be satisfied only by a combined approach to the problem, which presupposes a high level of organisation of the fuel combustion process in the engine cylinders, electronic control of the engine, the availability of lead-free fuel, and the appropriate level in the industrial manufacturing process, servicing, and the application of extremely effective devices such as catalytic converters.

II. Catalysts

In the practice followed in the leading foreign countries, the exhaust gases from internal combustion engines are purified in catalytic converters. A large number of catalytic reactions take place

on the detoxificiation catalysts for the exhaust gases from automobiles, for example:

$$CO + {}^1/_2O_2 \rightarrow CO_2, \quad (1)$$

$$C_nH_m + (n + m/4)O_2 \rightarrow nCO_2 + (m/2)H_2O, \quad (2)$$

$$H_2 + {}^1/_2O_2 \rightarrow H_2O, \quad (3)$$

$$CO + NO \rightarrow {}^1/_2N_2 + CO_2, \quad (4)$$

$$C_nH_m + 2\,(n + m/\Delta)NO \rightarrow (n + m/\Delta)N_2 + m/2H_2O + nCO_2, \quad (5)$$

$$H_2 + NO \rightarrow {}^1/_2N_2 + H_2O, \quad (6)$$

$${}^5/_2H_2 + NO \rightarrow NH_3 + H_2O, \quad (7)$$

$$2NO + 5CO + 3H_2O \rightarrow 2NH_3 + 5CO_2, \quad (8)$$

$$2NO + CO \rightarrow N_2O + CO_2, \quad (9)$$

$$CO + H_2O \rightarrow CO_2 + H_2, \quad (10)$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 2H_2. \quad (11)$$

The key reactions among the processes listed above are the oxidation of CO [reaction (1)] and of hydrocarbons [reaction (2)] to CO_2 and the reduction of nitrogen oxides by carbon monoxide to molecular nitrogen [reaction (4)]. Under non-stationary conditions, where the temperature of the exhaust gases varies from 200 to 1000 °C and the mixture composition varies from an oxidising mixture (with an excess of O_2) to a reducing mixture (with a deficiency of O_2), the best and virtually the only catalysts available, despite their high cost, are noble metals: platinum, palladium, ruthenium, and rhodium. In terms of their activities in the three main reactions, they can be arranged in the following way:[3]

Reaction	Catalysts
$CO+O_2$	$Pd \approx Rh > Pt > Ru$
$C_nH_m+O_2$	$Pt > Pd,\ Rh > Ru,$
$NO+CO$	$Ru > Rh > Pt > Pd.$

In terms of the complete set of catalytic properties, rhodium occupies the first place. However, it is very expensive—not more than 2.5 tonnes of rhodium are produced annually throughout the world. For this reason, the main component of catalytic converters (after-burners) is platinum, more rarely palladium, their overall production exceeding 100 tonnes. For the majority of reactions, platinum is more active than palladium but it is approximately twice as expensive. The main exporters of platinum metals on the world market are the USSR and the Republic of South Africa.[2]

The active component (a noble metal) is deposited on the oxidant (aluminium oxide), while the latter is deposited on a ceramic block in an amount of approximately 0.1%. For an overall weight of the catalyst of about 1–2 kg in one converter, this entails the consumption of 1–2 g of platinum.

There are two main types of converters: the straight-flow converter in which the exhaust gas passes through thin (0.5–1 mm) straight channels in a catalytic block with the deposited catalyst and a Z-shaped converter in which the catalyst, in the form of spherical pellets coated by the active mass, is exposed to the exhaust gases. Catalysts of the first time are being developed, for example, by the Engelhard Company and are used by the Ford Automobile Company. Catalysts of the second type are manufactured by the UOP Company and are used by the General Motors autombobiles.

The overall cost of the catalysts used in automobile after-burners is at present about one-third of the total cost of the catalysts manufactured throughout the world. The sharp increase in the cost of catalysts for the purification of automobile exhaust gases which occurred in 1988 is noteworthy. New stricter norms for the emission of harmful waste were introduced in Western Europe in that year.

Cost of catalysts manufactured throughout the world

	1987	1988
Petrochemical industry	620 million dollars	650 million dollars
Chemical industry	570 million dollars	600 million dollars
Automobile industry	330 million dollars	485 million dollars
Total	1520 million dollars	1735 million dollars

About 4 billion dollars have been spent on the development of catalytic converters by U.S. firms. At the same time, in the USSR controversy has continued as to the desirability of using converters, which are fitted throughout the world to more than 100 million automobiles with appropriate systems, about half of the world's consumption of noble metals being consumed in their provision.

In the development of catalysts during the 1970s, attention was concentrated on the possibility of eliminating hydrocarbons and carbon monoxide from exhaust gases with their aid. To ensure the complete combustion of these impurities, the catalysts must operate in the presence of a slight excess of air in the so-called "lean" mixtures with the stoichiometric coefficient $\alpha = [O_2]/[\Sigma C_nH_m] = 1.0-1.05$. In "rich" mixtures ($\alpha < 1$), the degree of conversion of hydrocarbons and carbon monoxide is sharply reduced.

A similar study of the kinetics of the reduction of NO_x by carbon monoxide, carried out, in particular, at the Institute of Chemical Physics of the USSR Academy of Sciences[4] on platinum and rhodium catalysts, showed that the opposite behaviour is observed for reaction (4); complete conversion is ensured in "rich" mixtures with $\alpha < 1$, while with increase in the oxygen content in the mixture it falls sharply. Only within a narrow concentration range (near stoichiometry) is there a "window" in the vicinity of which it is possible to achieve with a high degree of completion both the oxidation of carbon monoxide and hydrocarbons and the reduction of nitric oxide. The width of the "window" has come to be characterised by the quantity Δ (Δ is the range of variation of the oxygen content in the products resulting from the mixture in which all three reactions can occur with a high degree of convesion). Data[5] for the width of the "window" for different catalysts are presented below:

Catalyst	Ru	Pd	Pd–Ru	Pt	Pt–Rh	Pt–Pd–Rh
Δ, %	0.08	0.1	0.13	0.20–0.26	0.32–0.4	0.44–0.5

As can be seen from these data, binary and ternary catalysts are more effective in the elimination of all impurities than monometallic catalysts. In practice Pt–Rh catalysts are most often employed. However, owing to the high cost of rhodium, attempts have been made to reduce its content, i.e. to create compositions made up of platinum and rhodium in which rhodium would continue to exhibit its promoting effect even though its amount has been reduced. It has been possible to obtain effective catalysts with the ratio Pt : Rh = 15 : 1.

The study of the mechanism of the NO + CO reaction by spectroscopic-kinetic methods *in situ* (during catalysis), carried out at the Institute of Chemical Physics of the USSR Academy of Sciences,[4,5] showed that CO_2 and NCO groups can be identified on the catalyst surface under the conditions of the catalytic reaction.

On the basis of these investigations, the following mechanism of the NO + CO reaction was proposed:

$$NO + M_1 \rightleftarrows M_1{-}NO,$$
$$CO + M_1 \rightleftarrows M_1{-}CO,$$
$$CO + M_2 \rightleftarrows M_2 - CO,$$
$$NO + M_2 \rightleftarrows M_2{-}NO,$$
$$M_2 + M_2{-}NO \rightarrow M_2{-}N + M_2{-}O,$$
$$M_2{-}N + M_2{-}CO \rightarrow M_2{-}NCO + M_2,$$
$$M_1 + M_2{-}NCO \rightleftarrows M_1{-}NCO + M_2,$$
$$M_1{-}NCO + M_1{-}NO \rightarrow M_1{-}CO + N_2 + M_1,$$
$$M_1{-}CO + M_2{-}O \rightarrow M_2{-}CO_2 + M_1,$$
$$M_2{-}CO_2 \rightarrow CO_2 + M_2,$$

where M_1 are metallic centres on which NO molecules are adsorbed in the undissociated form and M_2 are similar centres on which NO molecules are adsorbed in the dissociated form. The key intermediate species is in this instance apparently the isocyanate NCO which can be adsorbed both on the metal (2240 cm^{-1} IR band) and on the carrier (2260 cm^{-1} band). The NCO groups can diffuse from the metal to the carrier and back again. The decomposition of NCO results in the formation of N_2. In the steady (stationary) state, the concentration of NCO adsorbed on the carrier does not enter into the kinetic equation. However, the real process in catalytic after-burners is markedly non-stationary. In a non-stationary process it is in fact important to have reserves of NCO stored on the carrier, which diffuses to the active centres of the metal and ensures the continuous reduction of NO to N_2.

Catalysts ensuring the removal of all harmful impurities (CO, C_nH_m, and NO) are referred to as three-component catalysts (it would be more correct to call them three-pathway catalysts) or bifunctional catalysts. Their composition is as a rule more complex than that of the catalysts designed solely for oxidation. Furthermore, in automobiles fitted with catalytic converters there are special electronic devices regulating the composition of gases so that they are close to stoichiometry.

After a time, the efficiency of the catalyst falls. The principal causes of the deactivation of platinum and rhodium catalysts are as follows:

(1) sintering after prolonged operation whereupon the size of the platinum and rhodium single crystals increases from 10–50 to 1000–5000 Å.

(2) the formation of higher oxides in an oxidising atmosphere, for example of Rh_2O_3, which reacts with the carrier to form $RhAlO_3$;

(3) the separation of the catalyst into layers, which leads, in particular, to the concentration of rhodium in the surface layer;

(4) poisoning (Pb, S, Zn, and P poisons).

The most important factor in the USSR is de-activation as a result of poisoning by lead, which is present in ethylated petrol. Non-ethylated petrol is used only in several large cities (Moscow, Leningrad, Kiev, and Alma-Ata). However, even in these cities it is difficult to avoid filling car fuel tanks with ethylated petrol anywhere outside the cities and this results in the deposition of lead on the catalyst surface and puts the converter out of order.

As a result of much research carried out by a number of firms, it has been possible to reduce appreciably the content of noble metals in catalysts for the purification of exhaust gases by introducing various additives, in some cases up to 0.1–0.2 g. The following are the main stabilising additives: SiO_2, CeO_2, SnO_2, BaO, and Cr_2O_3, whose role is to prevent the sintering of metal particles, and also additives which provide oxygen (CeO_2, MoO_3, WO_3, etc.). It appears that additives of this type are especially important for the operation of the catalyst under non-stationary conditions. It has been shown at the Institute of Chemical Physics of the USSR Academy of Sciences[6] that, when the $Pt + V_2O_5$ system is used, it is possible to reduce appreciably the temperature of the onset of the oxidation of methane. Under these conditions, the non-equilibrium V_2O_5 oxide phase is produced and on it oxygen is rapidly transported to the hydrocarbon oxidation centres. Such systems are very important for initiating the operation of the catalyst at a low temperature. The composition of one of the catalysts used by the Ford Company is as follows: 19% Al_2O_3, 1.6% NiO, 0.7% CeO_2, 0.15 Pt, an 0.015% Rh. Here CeO_2 is apparently both a stabiliser and an oxygen supplying agent.

Silicate systems are usually employed as carriers in the catalyst: cordierite $Al_4Mg_2Si_5O_{18}$, mullite $3Al_2O_3.2SiO_2$, and spodumene $LiAl(SiO_3)_2$. Cordierite is most common. Aluminium oxide (corundum — α-Al_2O_3) is sometimes used directly without decomposition on a silicate support.

The ShPK-2, ShPAK-0,5, and other catalysts, developed at the Karpov Physicochemical Institute and the Institute of Organic Catalysis and Electrochemistry (IOCE) of the Academy of Sciences of the Kazakh SSR jointly with NAMI, are used in the Soviet Union. The active component of the catalyst is platinum and palladium deposited on Al_2O_3 spherical pellets thermostabilised by added silicon, calcium, lanthanum etc. oxides. Experimental-industrial batches of the catalysts are produced by the Redkinsk factory.

Catalysts on metallic block carriers with a honeycomb structure are also being developed. Work on catalysts of this group has been carried on at the IOKE of the Academy of Sciences of the Kazakh SSR. The production of laboratory batches of metalic block carriers has been initiated at this institute and methods for depositing the support on the walls of the block channels (to increase the specific surface) and of depositing the active component on the carriers prepared in this way have been developed.

At the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences, catalysts on ceramic block carriers (made of spodumene, cordierite, and silicon nitride) are being developed jointly with other organisations. The blocks have a high mechanical strength (resistance to wear) and a reduced hydrodynamic resistance.

Catalytic converters are being developed and are being tested in the USSR by the Central Institute of Motor Construction Engineering (for diesel engines) and by the Automobile Engine Research Institute (NAMI) for petrol engines. The tests are performed on engine stands, stands with revolving drums, and under operating conditions on automobiles themselves.

The mass production of catalytic converters in the USSR has not yet been initiated. Several years ago, an experiment was carried out in Moscow: 600 taxicabs were fitted with catalytic converters. The experiment failed completely; firstly, it was not possible to prevent the introduction of ethylated petrol into the fuel tanks, which resulted in the poisoning of the catalyst, and, secondly, fires were started because in a number of engines the ignition did not work properly. For this reason, the uncombusted fuel entered the after-burner, was ignited on the catalyst, spoilt the after-burner, and sometimes set the engine on fire as well.

Thus the necessary conditions for the successful operation of catalytic converters is a thoroughly tuned engine with properly functioning ignition and non-ethylated lead free petrol.

3. Diesel fuel

Despite the widely held view that the toxicity of the spent gases from diesel engines is low, the problem of the protection of the environment from this source of emission should apparently be assessed as at least comparable to the problem of the pollution of the atmosphere by the spent gases from carburettor (petrol) engines, and, as transport fleets are increasingly provided with diesel engines and the study of the composition of the products of the combustion of diesel fuel intensifies, the urgency of the problem of their detoxification is becoming increasingly more acute and self-evident. Indeed, the amount of waste comprising the incomplete combustion products for which norms have been specified — carbon monoxide and hydrocarbons — generated by diesel fuels is smaller by a factor of 5–10 than that generated by carburettor engines, while the amount of waste comprising nitrogen oxides is similar. However, diesel engines eject into the atmosphere considerable amounts (on average 0.3–0.5 g m^{-3}) of soot — disperse particles which contain biologically active and toxic components, among which there is a group of carcinogens (benzopyrene, fluoranthene, chrysene, etc.), aldehydes, sulphur, nitrogen-containing organic compounds, inorganic sulphur compounds, etc.[7]

Despite the ambiguity of the results obtained in the study of the emission of these compounds by engines of different types, the leading role of diesel engines in polluting the atmosphere by disperse particles is noteworthy. Thus, according to an estimate,[8] the contribution of diesel engines to the 24.6 million kg of disperse particles ejected annually into the atmosphere in Western Europe by automobile exhaust gases is 21.3 million kg. In addition to the enhanced biological activity and toxicity, the presence of suspended disperse particles in the atmosphere impairs visibility on motor roads, pollutes the regions adjoining the roads, etc. In estimating the overall balance in the pollution of the atmosphere by the exhaust gases from diesel engines, one should naturally take into account also the presence in the exhausts of components for which norms have been laid down — carbon monoxide and especially hydrocarbons. Finally, the increased emission by diesel engines of nitrogen oxides constitutes a serious danger to the environment and human health especially if one bears in mind the increased biological activity of carbon monoxide in the presence of nitric oxide. These considerations, combined with the well known tendency towards an increase in the fleet of diesel-engined motor cars, show that the purification of the exhaust gases from diesel engines constitutes a serious and extremely urgent problem whose solution would make it possible to improve significantly the ecological situation not only in sites with limited exchange of air — mine shafts, quarries, stores, ships' holds, etc. — but also in cities with intense motor traffic, where the fraction of automobiles and buses with engines of this type has been increasing steadily.

Neutralisation (conversion) in diesel engines can be achieved by catalytic oxidation, filtration, or a combination of both methods. In addition, the application of these processes to the diesel engine is complicated by a number of factors due to the specific features of the operation of the antitoxic devices in the exhaust tract of the diesel engine. Among them the following should be included:

the relatively low temperature of the spent gases, which usually does not exceed 300–400 °C even under supercharged conditions;

the presence in the gas stream of fairly high (0.2–0.6 vol.%) concentrations of sulphur oxide compounds (mainly sulphur dioxide) and nitric oxide (0.1–0.2 vol.%), which are comparable or actually higher than the concentration of carbon monoxide;

a very considerable (up to 0.5 g m^{-3}) content of disperse particles of diesel soot in a number of instances (when the quality of the tuning of the fuel injection is inadequate) supplemented by aerosols comprising uncombusted fuel;

an increased emission of the degradation products of motor fuels, including the additives introduced into the fuel (the loss of oil in diesel engines is about 0.5% of the consumption of the diesel fuel, which is approximately 1.5–2.0 times greater than in carburettor engines);

strict requirements as regards the resistance of the exhaust system in modern and especially turbocharged diesel engines (the pressure drop in the exhaust system is limited to 500 mm of water).

These features of the design and of the working process in diesel engines have a significant influence on oxidation catalytic processes as well as filtration processes and must be taken into account in selecting and assessing the components, especially catalysts, used to purify the exhaust gases from a diesel engine.

As regards the operating conditions of diesel engines in the USSR, sulphur creates the greatest problems. Here we may note that almost the entire petroleum extracted in the USSR contain considerable amounts of sulphur and our industry (as well as science) is concerned with the catalytic hydrodesulphurisation, which appreciably lags behind foreign countries. Admittedly, one should note that the sulphur dioxide emitted with fuel combustion products in diesel engines makes a relatively small contribution (1–3%) to the overall pollution of the atmosphere by sulphur dioxide (thermal electric power stations make the main contribution). However, the oxidation of sulphur dioxide on a catalyst results in the formation of the appreciably more toxic sulphur trioxide, whose reaction with Al_2O_3 converts the latter into the sulphate, which leads to rapid breakdown of the catalyst.

A large series of studies on the selection of active oxide catalysts for catalytic converters has been carried out at the Azizbekov Azerbaijan Petrochemical Institute.[9] Studies are also being prosecuted at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences and at the Institute of Chemical Physics of the USSR Academy of Sciences. Sulphates leading to the breakdown of the catalyst are formed in almost all the oxide compositions. The development of oxide catalysts in Bulgaria has been reported.

It is noteworthy that the attempts to replace noble metals in converters in both petrol and diesel engines for the removal of harmful gases by a system comprising the oxides of transition metals or other elements have so far proved unsuccessful, mainly because of their being poisoned by the components of the exhaust gases and because of their low activity at low temperatures. The results in this field cannot nowadays be regarded as even hopeful to any extent.

In the USSR, catalytic converters for diesel engines are manufactured in small numbers using platinum and palladium catalysts (of the type ShPK and ShPAK). However, the Al_2O_3 forming part of their composition is rapidly converted into $Al_2(SO_4)_3$, which can be washed away by water on regeneration. After 2–3 regenerations, the converter becomes unsuitable. Despite their short lifetime, such converters are nevertheless used in highly gas-saturated closed spaces and in deep quarries.

There are certain prospects of being able to use aluminosilicates to create carriers with an increased resistance to sulphur oxides, but the choice of the optimum ratio of SiO_2 and Al_2O_3 makes it necessary to take into account, apart from the minimum capacity for conversion into sulphate, a number of other properties: strength, surface, resistance to water vapour, etc. It is possible to use other compounds, which do not interact with sulphur trioxide—phosphates, oxygen-free silicon compounds, etc.

The removal of soot is also a difficult problem. The planned standards for the emission of disperse soot particles are 0.16 g km^{-1} in 1989 and 0.12 g km^{-1} in 1992 for light automobiles and 0.6 g kW^{-1} h^{-1} in 1988 and 0.14 g kW^{-1} h^{-1} in 1994 for goods vehicles and buses with diesel engines.[10]

Taking into account the extremely high sensitivity of diesel engines to the resistance of the exhaust system and also the fairly strict requirements which must be met by the weight and size characteristics of the antitoxic devices, the creation of soot filtering systems for the latter presupposes the solution of a set of problems, including those concerning materials and catalysis:

(1) the choice of a material and of a technology for the construction of a filter from it subject to the permissible resistances, temperature, resistance to the action of the components of the spent gases, strength characteristics, porous structure, soot trapping efficiency, etc.;

(2) the search for catalysts capable of reducing by 200–300 °C the temperature of the combustion of the soot accumulated by the filter, ensuring thereby the regenation of the filter by means of the heat of the spent gases;

(3) the development of filter-catalytic devices ensuring in a single space the after-burning of the incomplete combustion products as well as the trapping of the soot.

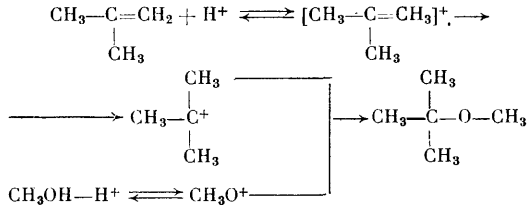
Apart from the problem of creating a filtering material, it is in this instance necessary to solve the problem of depositing a support (meeting the requirements as regards the pressure drop on the filter) and of the regulation of the soot regeneration (combustion) process in order to eliminate the superheating of the catalyst. It is also necessary to develop methods for increasing the useful lifetime of the catalyst and the filter in which provision is made for protection against the ash products of the combustion of soot.

4. Alternative fuels

Tetraethyl-lead, used as the antiknock additive, is a highly toxic component of petrol. One of the versions of the causes of the destruction of the Roman Empire is the poisoning by lead of its inhabitants who used water from lead pipes. This led to apathy of the inhabitants and the consequent destruction of the empire under the onslaught of barbarians. Lead acts on the human nervous system and is not eliminated from the organism. Furthermore, lead compounds have a destructive effect on nature in territories adjoining motor highways.

There exist two main ways of creating metal-free high-octane fuels: (1) by increasing the degree of catalytic processing of the products of the primary distillation of petroleum: cracking, reforming, etc.; (2) by using metal-free antiknock additives. In the USA, studies are being prosecuted mainly via the first route, whilst in Europe the second route is followed. Certain firms (for example, ENI—Italy) have carried out a wide scale screening of newly synthesised organic compounds as antiknock agents. In the USSR, studies on such a scale have not been performed.

The most widely used antiknock agent in the West is t-butyl methyl ether (TBME). It is synthesised using acid catalysts:



The side reactions accompanying the synthesis of TBME are as follows:

$$\text{iso-}C_4H_8 + H_2O \rightleftharpoons (CH_3)_3COH,$$
$$2CH_3OH \rightleftharpoons H_2O + CH_3OCH_3,$$
$$2\text{iso-}C_4H_8 \rightleftharpoons C_8H_{18} \longrightarrow \text{polyisobutenes},$$
$$CH_3OH + \text{iso-}C_4H_8 \rightleftharpoons CH_3OC_4H_9.$$

Catalysts of the synthesis of TBME include gel cation exchangers (KQ-2, FPP), heteropolyacids ($H_3PW_{12}O_{40}$/activated charcoal), H-acids [sulphonic acids, H_2SO_4, HCl, and HNO_3 (70–150 °C)], zeolites, Al_2O_3, $Al_2O_3.SiO_2$, and P_2O_5/Al_2O_3 (60–250 °C). In the presence of some of them, it is possible to achieve a selectivity close to 100%. Methods for the continuous catalytic synthesis of TBME using zeolites (Tseokar-2) or toluene-*p*-sulphonic acid have been developed at the Institute of Chemical Physics and at the Institute of Organic Chemistry at the USSR Academy of Sciences. Methods for the synthesis of TBME are being developed at the Institute of the Ministry of Petrochemical Industry. However, the large scale manufacture of TBME in the USSR is not planned to start until 2000–2005.

The decrease of the octane number of petrol, induced by the decrease in the content of lead and aromatic hydrocarbons, is fully compensated by the addition of 5–15% of TBME. The use of TBME also constitutes a very rational procedure for the indirect introduction of methanol into petrol. The problems of phase separation, occurring in petrol–methanol mixtures, do not then arise.

The manufacture of TBME in the USSR requires an increase in the manufacture of methanol. This can be achieved by using a new productive method of synthesis of methanol developed at the Institute of Petrochemical Synthesis of the USSR Academy of Sciences.[12]

Using a procedure similar to that for the synthesis of TBME, it is possible to obtain from tertiary C_5 olefins the tertiary methyl pentyl ether, which has certain advantages over TBME as an antiknock agent.

A disadvantage of such antiknock agents is the presence of oxygen atoms in their molecules. The combustion of the ethers results in the formation of toxic aldehydes.[13,14] In the norms for the emission of toxic products, aldehydes are so far in no way regulated and this also applies to carcinogens of the type of benzopyrene. This problem requires special study.

We are unable to consider here the problems of the toxicity of all types of automobile fuels. We may note that, whereas from the standpoint of economics this problem continues to be discussed, the systematic studies on fuels from the standpoint of ecology are clearly inadequate.

Studies on the use of light hydrocarbons as a petrol-substitute fuel have been expanded in recent years in many countries including the USSR. Thus an attempt has been made to use

propane–butane mixtures as a fuel. In recent press publications, it has been reported that the drivers and passengers of automobiles operating on the propane–butane mixture have been poisoned. This can apparently be accounted for by design faults and not by the higher toxicity of the combustion products. On combustion of the propane–butane fuel, the exhaust gases contain much less carbon monoxide and hydrocarbons, but the amount of NO_x is approximately the same as in the combustion of petrol.[13] However, it is hardly possible to supply the automobile fleet by large amounts of the propane–butane fuel. The situation is different as regards methane, the potential amount of which in the USSR is very great. At the present time methane is regarded as the No. 1 alternative fuel.

The combustion of light hydrocarbons in internal combustion engines is being investigated at the Institute of Chemical Physics of the USSR Academy of Sciences. It has been found that the emission of toxic products can be reduced by a suitable organisation of the combustion process in the engine.

The study of the ignition limits of ballast-containing hydrocarbon mixtures (containing combustion products and inert gases) demonstrated a distinct shift of the ignition region for hydrocarbons heavier than propane to richer compositions, while the ignition region for the only hydrocarbon lighter than oxygen (methane) was displaced towards leaner mixtures (although their composition is closer to stoichiometry). The study of the operation of a one-cylinder petrol engine with low filling (in reality the engine operates most of the time partial load conditions with low filling) also showed that stable operation with low filling (minimum scatter in pressure diagrams and the absence of missing in ignition) is recorded in the region of rich mixtures. These experiments indicate the influence of diffusion-thermal phenomena (roughly speaking the "selective" diffusion of the lighter, deficient mixture component) on the combustion process and that attempts to shift the range of stable operation to leaner composition in engines operating on petrol by increasing the energy of the discharge are doubtful. Studies prosecuted at the Institute of Chemical Physics of the USSR Academy of Sciences, using a discharge with additional charging, with plasma ignition, and using a "magnetic" spark plug led to the same result. Furthermore, the energy required to ignite rich propane mixtures is much lower than that required for the ignition of lean mixtures. Conversely, the energy is minimal for methane in lean mixtures. All this indicates the special role of methane as an engine fule. Methane has an octane number in excess of 100 and can be used for higher compressions (12–13 and above) and smaller cylinder diameters.

The possibility of the operation of engines on methane in lean mixtures eliminates the problem of the ignition of carbon monoxide and hydrocarbons. The problem of NO_x naturally remains. An important problem is the filling of cylinders and the storage of methane. The storage of methane in the compressed form in cylinders requires a large capital expenditure associated with the conversion of petrol filling stations into gas filling compressor stations. The use of compressed methane naturally limits the transportation distance. Experiments on the possibility of filling with methane cylinders containing an adsorbent—silica gel or activated charcoal—have been carried out at the Institute of Chemical Physics of the USSR Academy of Sciences.

The problem of the use of methane in internal combustion engines involves a number of questions associated directly with the engine. It is necessary to create an engine which operates on methane at a high compression. For this reason, it is impossible to employ the usual petrol engines. The use of methane at a low compression (7–8) is pointless. One can be satisfied with an intermediate version of the engine in which the compression is reduced from 12–13 to 7–8. It is possible to create a gas-diesel cycle at high compressions (>15–17) with injection of an igniting dose of fuel with a high octane number.

The opposite process is one involving the pre-chamber ignition of methane (a single fuel engine containing an injection apparatus only in the ignition system). It is also possible to introduce petrol and even heavy fuels (for example, with post-injection into a very lean methane–air mixture (for a coefficient of the excess of air of 5 and above, i.e. for a low consumption of methane).

Engines with precombustion chamber ignition, constructed at the Gorky Automobile Factory on the basis of designs developed at the Institute of Chemical Physics of the USSR Academy of Sciences, are used in the Volga motor cars. They achieve an appreciable reduction of the emission of carbon monoxide and hydrocarbons. For the wide scale introduction of high-octane fuels and catalytic converters, the manufacture of automobiles with precombustion chamber ignition may be a palliative solution. For this purpose, it is essential to continue the work at the Gorky Automobile Factory and the Institute of Chemical Physics of the USSR Academy of Sciences.

Hydrogen is an ecologically clean fuel. It can ignite over a wide range of concentrations and burns in very lean mixtures in the presence of a large excess of air. The maximum temperature developed in the engine and determining the formation of nitrogen oxides is therefore much lower than in the combustion of petrol and the oxides NO_x are hardly formed.[14] The exhaust gases contain no hydrocarbons and carbon monoxide. The only combustion product is water vapour.

The problem of hydrogen as a fuel for internal combustion engines has been widely discussed. At the end of the 1988, an international conference on hydrogen power engineering was held in Moscow.[15] At the present time, the remaining problem is the high cost of hydrogen and the difficulty of storing it. However, in the XXIst century the cost of hydrogen will be such that its use will become justified not only from the ecological but also from the economic point of view, especially bearing in mind the high cost of cleaning the environment when other fuels are employed. Together with the gasification of coal, the promising processes for the preparation of hydrogen are apparently those where hydrogen is produced from the biomass.[15] An interesting method is the preparation of hydrogen by decomposing hydrogen sulphide. Before the industrial development of such a process, one should abandon the development of the Astrakhan deposit of natural gas and other hydrogen-containing gases.

Hydrogen for use in internal combustion engines may be stored in compressed and liquefied forms and as part of hydrides. At the present time, liquid hydrogen is most promising, but there is as yet no final technical and economical solution.

In the USSR, the problem of using hydrogen as a fuel for internal combustion engines is a major concern of the Institute of the Problems of Machine Construction of the Academy of Sciences of the Ukrainian SSR (Kharkov). The involvement of specialists in catalysis in the problem of hydrogen power engineering is clearly inadequate.

A version of the use of hydrogen in internal combustion engines may involve the employment of fuels generating hydrogen on decomposition. For example, methanol produces the $CO+2H_2$ mixture on catalytic decomposition. This mixture burns at high rates for very lean compositions (the diffusion-thermal phenomena in hydrogen are especially pronounced for lean compositions) and for

this reason this version is also ecologically interesting. A catalytic reactor for the decomposition of methanol may be placed before the combustion chamber and can be heated by the combustion products.

An alternative to the proposed variants may be the abandonment of the automobile as a means of transport in the XXIst century.

For the successful prosecution of the relevant studies in the USSR, the following steps are necessary:

1. The creation of a qualifying commission made up of scientists and engineers of the USSR Academy of Sciences and government departments for the systematic examination of the prospects for the manufacture of automobile fuels from the standpint of ecology.

2. An appreciable expansion of theoretical studies at the Institutes of the USSR Academy of Sciences on catalytic conversion, particular attention being devoted to the mathematical modelling of non-stationary catalytic processes in engines, the study of elementary processes in the conversion of carbon monoxide, hydrocarbons, nitrogen oxides, and ammonia by physicochemical methods *in situ*, and the development of conversion processes in the presence of oxygen. It is necesary to devise a theory of the effect of additives increasing the efficiency of noble metals as oxidation catalysts.

3. The development of longer-lived catalysts resistant to the action of poisoning impurities (sulphur dioxide, lead, etc.) and further studies designed to reduce the content of noble metals in catalysts and their complete or partial replacement by oxide systems whilst retaining the required level of efficiency and useful life.

4. The development of catalyst carriers (monolithic and granular) with a required level of hydrodynamic, mechanical, and physico-chemical characteristics and resistant to the action of catalytic poisons. Their production in the USSR should be initiated.

5. The development of methods for the regeneration of catalysts containing noble metals.

6. The organisation of the industrial manufacture of catalysts to provide catalytic converters for petrol and diesel engines.

7. The improvement of the design of internal combustion engines and the introduction of oxygen sensors and electronic systems for the control and regulation of fuel compositions.

8. The provision of the promoter of catalysts with the necessary amount of compounds of precious metals. The limitations to the use of platinum should be removed.

9. The development of methods for the removal of disperse particles from exhaust gases, including catalytic methods for the after-burning of soot on filter elements.

10. An increase in the number and accessibility of tests of catalytic converters on automachines, including comparative tests; the provision of foreign currency for the purchase of the best foreign designs.

11. The creation of a program of toxicological tests on the products of the combustion of various fuels, including oxygen-containing fuels.

12. The achievement of the strict fulfilment of the standard norms of the UNO and the USSR as regards the emission of toxic substances. Economic measures stimulating the use of antitoxic devices (for example, penalities for harmful emissions, and conversely, a decrease in the price of automobiles fitted with a catalytic converter) should be introduced. The question of the introduction of norms for the emission of aldehydes and carcinogenic hydrocarbons should be raised.

13. The submission to the government of the USSR of the proposal to accelerate the large scale manufacture of methanol and TBME.

14. The organisation of the mass screening of organic compounds for the antiknock properties in order to replace tetraethyl-lead in petrol.

15. The expansion of theoretical studies on the combustion of various fuels in automobile engines. A well equipped centre for problems of combustion should be created.

16. The examination of the problem of the need to create a high-compression methane engine.

17. The expansion of the manufacture of engines with precombustion chamber flame ignition for the rapid solution of the problem of reducing harmful exhausts in the immediate future.

18. Theoretical and experimental study of the use of adsorbents to concentrate methane in cylinders.

19. An appreciable intensification of research into the combustion of hydrogen in engines and on catalytic, photochemical, electrochemical, thermal, and biological methods for the production of hydrogen and its storage in a liquefied or bound form. The prospects for using hydrogen in internal combustion engines should be widely discussed and the participation of catalytic laboratories in the solution of this problem should be increased.

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Development and introduction of catalytic methods for the detoxification of industrial and automobile transport waste emissions

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New technologies based on the use of chemical catalysis should play an important role in the solution of acute ecological problems. Firstly, these are the catalytic technologies for the detoxification of the largest amounts of waste emissions from industry and automobile transport. Secondly, these are new technologies, producing little waste, for the manufacture of chemical products and based on the use of more selective catalysts.

The catalytic technologies for the detoxification of gases and liquid waste from various branches of industry and automobile transport, developed by the "Katalizator" Interbranch Scientific-Technical Complex, will be examined below. Their wide scale employment in the existing undertakings and in transport could even today improve significantly the ecological situation in our country.,

1. Elimination of sulphur dioxide from the waste gases in non-ferrous metallurgy

The emission of sulphur dioxide by non-ferrous metallurgical industries is one of the principal sources of the formation of acid rain. The "Katalizator" Scientific-Technical Complex is developing, jointly with the organisations of Ministry of Metallurgy of the USSR, several technologies for the removal of sulphur dioxide from such gaseous emissions with the simultaneous manufacture of valuable products — sulphuric acid or elemental sulphur. Some of these developments are significantly superior to those abroad as regards the level of their sophistication.

A non-stationary method (the flow reversal process) for the removal of sulphur dioxide with the simultaneous manufacture of sulphuric acid has been developed. This new technology is suitable for the majority of regions in the USSR. It is applied on an industrial scale in a number of factories. With the aid of this technology, more than 300 000 tonnes of sulphuric acid annually is already being produced† and is finding useful applications in the national economy. Licences for the flow reversal process for the oxidation of sulphur dioxide have been taken up by firms in Japan and Bulgaria.

Catalysts and processes for the conversion of sulphur dioxide into sulphur are being developed for the detoxification of the waste gases from the Noril'sk Mining-Metallurgical Industrial Unit. The conversion of sulphur dioxide into sulphuric acid under the conditions of the Noril'sk establishment is not appropriate because of the difficulties in transporting it away. Sulphur can be obtained by the partial reduction of sulphur dioxide to hydrogen sulphide, after which the catalytic Claus process is carried out. This process can be achieved in the presence of both heterogeneous and homogeneous catalysts. Both heterogeneous and homogeneous catalysts of the Claus process, specially developed for the Noril'sk Mining-Metallurgical Industrial Unit, have already been tested experimentally in the latter. The characteristic features of the new heterogeneous catalyst are improved activity (as a result of this, it is possible to reduce significantly the size of the catalytic apparatus) and also resistance to the oxygen present in the waste gases from the unit. The manufacture of a large batch of this catalyst for experimental-industrial tests is being prepared.

A method for the removal of sulphur dioxide from waste gases is being developed on the basis of the new homogeneous catalyst — the so called LES‡ (liquid-phase elimination of sulphur) process. At the present time this method is being tested on a large scale experimental apparatus in Noril'sk.

2. Elimination of nitrogen oxides from the waste gases from chemical industries and thermal electric power stations

A new catalytic method is being developed for the reduction of nitrogen oxides by ammonia under artificially created non-stationary conditions (a variant of the flow reversal process). An experimental-industrial apparatus with an output of 10 000 $m^3\ h^{-1}$ has been constructed and has been working successfully.

A variant of the flow reversal process for the selective catalytic reduction by ammonia of nitrogen oxides in the waste gases from thermal electric power stations is being developed.

3. Elimination of hydrogen sulphide from natural gas

The natural gas from a number of large deposits in the USSR contains considerable admixtures of hydrogen sulphide. The method for its elimination used at present is fairly complex. It is based on the partial oxidation of hydrogen sulphide to sulphur oxides followed by the multistage Claus process. The "Katalizator" Interbranch Scientific-Technical Complex has been developing jointly with the organisations of the Ministry of the Gas Industry of the USSR a fundamentally new single-stage purification technology involving the catalytic oxidation of hydrogen sulphide to elemental sulphur. The method has passed an experimental test in the detoxification of the so called blow-off gases from bore holes.

4. Elimination of carbon monoxide and organic substances from industrial waste gases

An appreciable amount of carbon monoxide and a wide variety of organic compounds is present in the waste gases from ferrous metallurgical and chemical industries. Harmful organic substances

† February, 1989.

‡ SOZh in Russian (Ed. of Translation).