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Test of catalysts for purification of toxic gases of the motor transport and the industry

Abstract: The work aim was preparation and testing effective catalysts for reduction of toxic gases of the motor transport and industry. The laboratory flowing installation, the stationary diesel generator of brand 5GF-LDE with power of 5 kVA and the diesel engine – generator of Kama Automobile Plant truck running on diesel fuel were used for investigation. The full-sized catalysts were also used for the experimental – industrial tests of catalysts with JSC "EMG" (Kazakhstan) on flue gas of oil heating furnaces in order to reduce toxic emissions. Stability of the carriers and the active phases to poisoning by water vapour was researched. The tests showed high efficiency of the neutralization on NO_x- to 65%, C_xH_y-to 85.0-88%, CO-99.0-100%. The catalytic samples on the basis of Ni and Mn promoted by Pd (0.1%, 0.25%) and Pt (0.1%), provide high degree of transformation CO to CO_2, C_xH_y into CO_2 and H_2O, NO to N_2. Decrease in toxiferous emissions on the South-West Kamyshitovoye field was: on CO –100%, on NO -7.7%, on NO_x-7,7%, on SO_2 – 57.1%; on the "S. Balgimbayevo" field: on CO – 99.6%, on NO -20.4 %, on NO_x-19.6 %.
Key words: catalyst, exhaust gases, metal block carriers, diesel generator

Introduction

In general, emissions of pollutants and greenhouse gases into the atmosphere from industrial activities and transport are formed from the emissions of stationary and mobile sources. Road transport emissions relate to emissions from mobile sources and are determined by emissions of vehicle pollutants during their transport operations. The source of emission of harmful substances of a motor vehicle is the internal combustion engine installed on it. In the exhaust gases of the engine contain more than 200 toxic chemical compounds [1, 2].

Except direct negative impact on health of the person, emissions of the motor transport have greenhouse and ozone-depleting effect on the atmosphere of the earth. It is connected with the content in the fulfilled gases of the engine of the following substances: carbon dioxide CO_2, the main component in the exhaust gases of the engine, creating a greenhouse effect in the atmosphere (greenhouse gas); methane CH_4, ammonia NH_3 and nitrous oxide N_2O – greenhouse and ozone-depleting substances contained in the exhaust gases of the engine. The qualitative and quantitative indicators of the release of harmful pollutants with exhaust gases of vehicles during their transport work are ambiguous and depend on many factors: on the type of the used fuel, from the design, conditions and operating conditions of the engine, on the amount of the done work, on the type and characteristics of the car's movement. Protection of the environment from industrial and transport pollution poses to humanity demands to improve the synthesis methods of neutralizing catalyst and purification of gas emissions from harmful [3-5]. The most effective means of purifying of the exhaust gases of internal combustion engines of automobiles is catalytic method. It's known that as primary catalyst carrier for neutralization of off-gases of motor transport and the industry use a metal wire, a steel foil, a grid from stainless steel or from bronze, the granulouse carrier – in the form of balls or extrudates, the ceramic carrier from a spodumen, oxide or zirconium nitride, etc. However not all of them are capable to maintain the loadings received in use in actual practice operation (on the car and in the production conditions), and also to correspond requirements imposed to catalytic converters such as thermal stability, mechanical strength, gas-dynamic resistance, stable catalytic activity throughout the progressive time of operation. Monolithic blocks are the most suitable carriers of the catalysts used for the solution of environmental issues [6, 7]. The development of compositions and methods of preparation of a new generation of

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catalysts with low content of platinum group metals for complex purification of exhaust gases of motor transport becomes more relevant in the world due to the deteriorating state of the atmosphere, especially in the industrial cities, and the tightening of environmental standards [8-10].

The work aim was synthesis of efficient and stable catalysts of neutralization of exhaust gases of motor transport on the metal block carriers and their test in the laboratory and in actual use on natural gases of the stationary diesel generator of brand 5GF-LDE with power of 5 kVA at various loadings and on the diesel engine of Kama Automobile Plant (KamAP). It was also planned to applicate the full-sized catalysts for the experimental – industrial tests of catalysts with JSC "EMG" (Kazakhstan) on flue gas of oil heating furnaces in order to reduce toxic emissions.

Materials and Methods

Preparation of the laboratory and full-size examples is carried out by earlier developed technique [11-14]. The primary carrier of catalysts is made of heat-resistant steel foil (corrugated and rolled into a block) brands H23Yu5, H15Yu5 containing about 5% aluminum, of 50.0 microns thick. The washcoat is a suspension of aluminium salt or of aluminium salt with additives.

The laboratory tests were carried out at the mounted laboratory installation (fig.1) with a tubular reactor of integrated type. Installation consists of the cylinders (1) containing researched gases (hydrocarbons, carbon oxide, nitrogen oxide, nitrogen). In system air was moved, gases were moved from cylinders, then through ventile of thin adjustment (3) entered to rotameter (4) individually calibrated under each gas and needed for gas speed regulation intended which then moved to the mixer (6) where gases were mixed up and entered to a quartz reactor (7) with diameter10 mm. The reactor was heated with by tubular furnace, the temperature in which was measured by chromele-alumele thermocouple (9). The reactor temperature was fixed by potentiometer, temperature regulator (11), calibrated by e.d.p. of thermocouples.

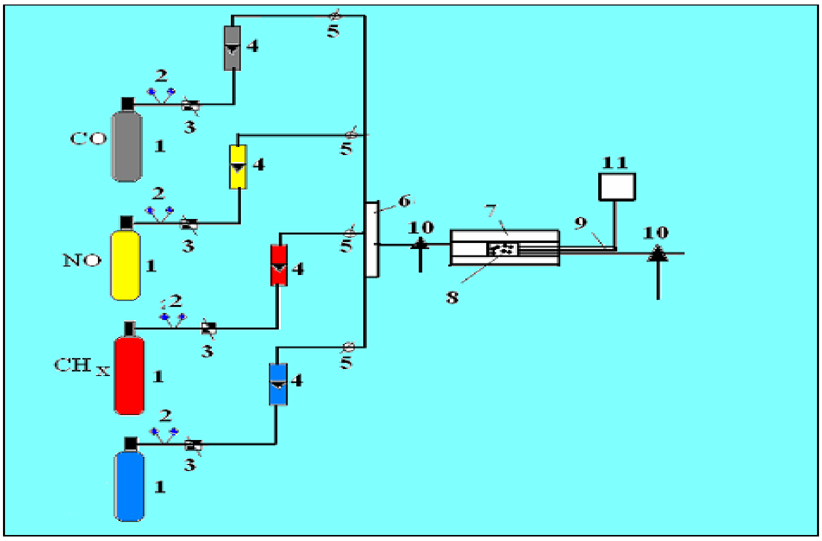


Figure 1 – Scheme of the flowing installation: 1- A gas bag; 2-Manometer; 3-Ventile of thin regulation; 4-Rotameter; 5-Crane; 6-Mixer; 7-Heating system; 8-Catalyst; 9-Thermocouple; 10-Selection of tests before and after the catalyst; 11 – Temperature regulator.

Gas mixture is prepared by giving into the mixer of hydrocarbons from a cylinder and compressed air from the line. Content of hydrocarbon in mix was 0.5 vol.%. Concentration of oxygen varied from 2.0 to 10.0 vol.%. The gas mixture was analyzed by GLC and OPTOGAZ gas analyzer before and after the reaction. The chromatographs "Crystal 2000M" and Chrom 3700 with a flame ionization detector were used. Time of analysis-20-30 min. Before testing, the catalyst sample was kept in the reactor for 30 min. in the flow of the reaction mixture at 500°C. Thereafter, the gas temperature was lowered to given values, and was determined the conversion of CO, NO and hydrocarbons.

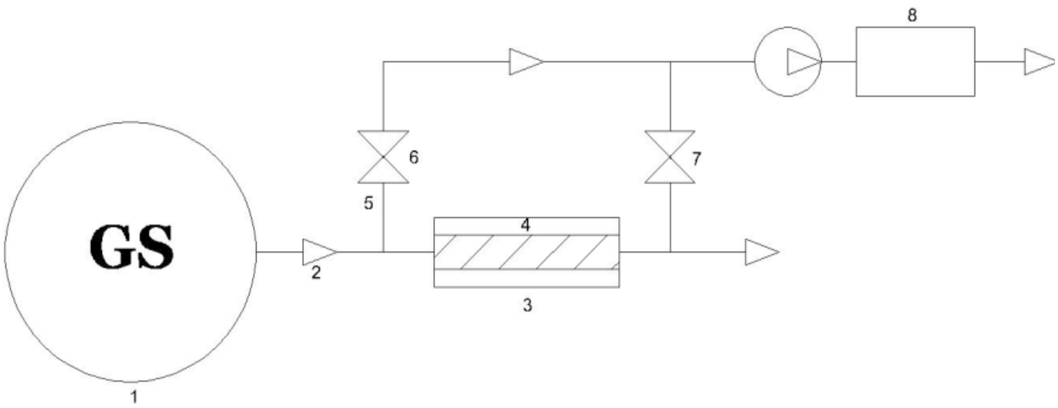
Characteristic of activity of the catalyst was the degree of conversion (α) of initial reagent (hydrocarbon, carbon monoxide, nitric oxide), defined by the formula:

$$\alpha = C\ init.-C\ fin./C\ init.\ \cdot 100\ \%,$$

where $C_{init.}$ and $C_{fin.}$- are the initial and final concentrations of a reagent in volume of a test.

The full-size samples of the block metal catalysts were used in the researches at the stand on the basis of diesel generator of brand 5GF-LDE with power of 5 kVA (fig.2, 3). The full-size catalyst samples had a diameter of 30.0 mm, a height of 90.0 mm. The catalyst was loaded into the gas-abstersive offshoot of the diesel generator. Temperature before and after the catalyst is determined with help of a chromel-alumel thermocouple outputted on the digital indicator. Gas mixture was analyzed by means of GLC and on a gas analyzer "Optogaz 500" before and after the reaction. The chromatographs "Crystal 2000M" and "Chrom 3700" with a flame ionization detector were used. Analysis duration was equal to 20-30 min.

Figure 2 – The catalytic unit (the stand) on the basis of diesel generator



1 – Diesel generator; 2 – exhaust pipe; 3 – catalytic reactor; 4 – catalyst sample; 5 – gas operated probe; 6, 7 – sampling valves before and after the catalyst; 8 – a gas analyzer.

Figure 3 – The general scheme of the bench on the basis of the diesel-generator

The full-sized catalysts were also used for the experimental – industrial tests of catalysts on the diesel engine of Kama Automobile Plant (KamAP). The object of a test – diesel engine – generator of KamAP of model 820.52-260- is completed with pistons of model 820.52-1004015-40 CB with the chamber of combustion in diameter of 80.0 mm, depth of 25.0 mm, cylinders heads of model 7406.1003040, turbo kompressors "Schweitzer" S2B/7624TAE with cases of turbines with A/R=1.0 and the complete set of the catalytic neutralizers which was elaborated by authors of this article. The neutralizer consists of 2 block catalysts on the metal carrier (fig.4) in diameter of 220 mm and height 90.0 mm everyone with the honey comb structure of channels. 0.1 weight. % Pt was used as an active component. The prepared catalyst was tested on the engine working on the diesel fuel with the characteristics: cetane number, not less – 49, density at 150°C-820-860, concentration of sulfur, not more than-500 ppm. In system of greasing oil "Lukoil Super" SAE15W40, APICF4 was used. As cooling liquid (freezing) water was applied. Definition of concentration of gaseous harmful emissions in the waste gases, including, nitrogen oxides (NO_x), total hydrocarbons (C_xH_y), carbon oxide (CO), was made by a multicomponent gas analyzer "Autotest – 02.03" of the I-st class. Calculation of specific emissions was carried out in view of power consumption at n=1500 rev/min., power consumption – 3.5 kVA, at n=2200 rev./min, power consumption – 11.2 kVA. Definition of harmful emissions in the exhaust gases on a minimal idle motion was carried out on the preliminary preheated engine in a mode of rated power.

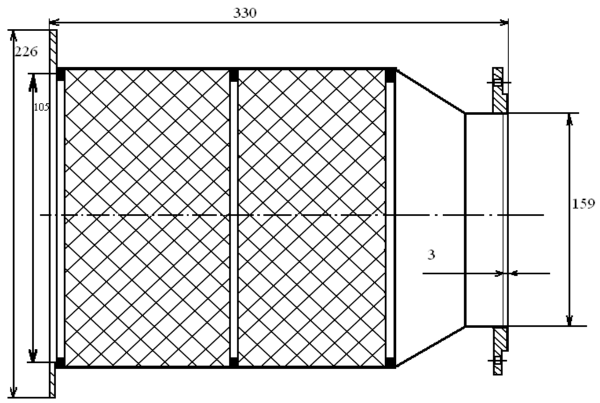


Figure 4 – Dimensions and the scheme of disposition of the catalytic neutralizer in the case

The full-sized catalysts on the block metal carriers were also used for the experimental – industrial tests of catalysts with JSC "EMG" (Kazakhstan) on flue gas of oil heating furnaces in order to reduce toxic emissions. Ready full-size catalysts on metal blocks entered on assembly where cylindrical corps were manufactured. In casings there are clamps for catalysts. Catalytic filters are installed directly on the pipe of waste gases of oil heating furnaces after the samplers before the catalyst (fig.5). In order to reduce heat transfer catalyst was wrapped with heat insulating mineral wool with reflective foil. In the course of operation of the furnace temperature of gases was determined before and after the catalyst by a mercurial thermometer and a temperature sensor of a gas analyzer. Concentration of toxiferous gases before and after catalytic filters was defined by a gas analyzer of MCI-150 of Bosh firm. Dimensions of the block filter is: for the furnace PTB-10/64: diameter – 410 mm, height 400 mm, for the furnace PT-16/150 – diameter -500 mm, height 400 mm, for the furnace PT-3.5 – 900 mm diameter, height of 400 mm. Temperature of off-gases on the S. Balgimbayevo field to the catalyst was in limits 350ºC.

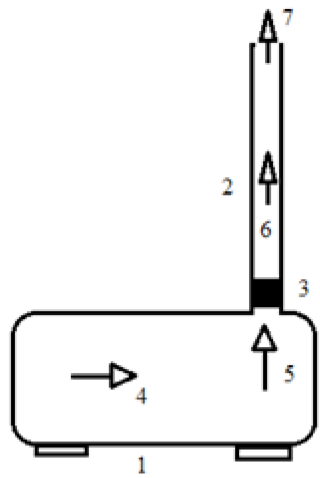


Figure 5 – Technological scheme of the installation and the functional principle of the catalyst in the furnace of oil heating: 1 – Furnace of oil heating, 2 – flue, 3 – catalytic neutralizer, 4,5 – stream of waste gases (CO, CH_x, NO_x) before the catalyst, 6,7 – the flow of gases after the catalyst (H_2O, CO_2, N_2).

Results and Discussion

The poisoning action of SO_2 in the process of cleaning of combustion gases was studied. XPS research of freshly prepared and waste (after the long-run tests of 50 hours) catalysts showed that the reason of decrease of the activity of the Pt-containing catalysts in the course of purification of products of combustion of fuel is associated to accumulation of sulfur compounds. Investigation of the activity of catalysts based on Pt, Pt + Pd, Pd on stability to SO_2 (0.1% in air for 10 hours at 350°C) showed that the catalyst activity is reduced at low test temperatures, but after calcination at 500°C with air blowing for 2 hours Pt catalyst activity is almost reduced and activity of the Pd-catalyst is reached to 80%.

Tests of full-sized samples of the catalysts were carried out on all modes of operation of the engine of the diesel generator (a no-load operation (idling), 1.0; 2.0; 3.0; 4.0 kVA). The results of triple tests of catalysts are presented in tab. 1, 2.

Catalysts based on palladium and platinum with a promoting additives were tested for thermal stability under load of diesel generator 3.0 kVA. During the 100-hour test with fractional neutralizers calcination at 600°C at an interval of 5 hours in a muffle furnace it was found that the introduced structural and textural thermostabilizing additives into the catalysts promote a sustainable activity (tab.3).

Table 1 – Reduction of the toxic emissions on the diesel generator with use of 3.0% catalyst on the basis of Mn and Ni oxides

Power consumption, kVA	The temperature of exhaust gases, °C	The content of toxic components in the exhaust gas, ppm					
		CO		C_xH_y		NO_x	
		Before catalyst	After catalyst	Before catalyst	After catalyst	Before catalyst	After catalyst
Idling (0)	25	0.036	0.035	65.0	60.0	13.2	13.2
2.0	260	0.030	0.00	81.0	20.0	17.4	10.8
3.0	300	0.021	0.00	89.0	3.5	19.0	7.6
4.0	425	0.014	0.00	111.0	10.0	23.0	8.0

Table 2 – Reduction of the toxic emissions of diesel generator by using a catalyst on the base of 0.2% Pd

Power consumption, kVA	Temperature of exhaust gases, °C	The content of toxic components in the exhaust gas, ppm					
		CO		C_xH_y		NO_x	
		Before catalyst	After catalyst	Before catalyst	After catalyst	Before catalyst	After catalyst
Idling (0)	25	0.033	0.033	67.2	55.1	14.5	14.1
2.0	533	0,03	0.002	79.6	62.3	17.8	8.3
3.0	573	0.02	0.00	92.1	6.4	21.0	6.4
4.0	698	0.015	0.00	107.0	4.2	22.6	7.0

Table 3 – Tests of thermal stability Pt- and Pd-containing catalysts on diesel generator

The catalyst	Exhaust gases	Initial degree of cleaning, %	Duration of testing, h.				
			5	10	25	50	100
0.1% Pt+Ni	CO	100	100	100	100	100	100
	C_xH_y	95.0	95.3	94.2	94.3	94.2	94.7
	NO_x	60.5	60.0	61.0	59.8	59.7	59.6
0.2% Pd+Mn	CO	100	100	100	100	100	100
	C_xH_y	90.0	90.2	90.0	88.7	88.8	88.4
	NO_x	48.2	42.9	48.1	48.1	46.8	46.4

It was found a presence of SO_3 and SO_2 in the exhaust gases of diesel-generator. On all the catalysts after the tests was observed the soot scurf, but least of all the carbon black content on zeolite-containing catalyst was presented. Also on the catalysts it was revealed phosphorus and less zinc oxide, apparently presenting in the diesel fuel in the form of organic additives. Nevertheless, the catalysts were resistant to poisoning by "poisons" contained in the exhaust gases. The most effective catalyst was a zeolite-containing carrier, promoted with Pt. Its effectiveness has remained constant for 50 h. of the diesel engine operation.

By the method of emission spectrum analysis the composition of the catalyst after 50 h. of operation on the diesel generator was studied. It was found the presence on the surface S, P, Zn, Ca, Mg. Probably, these elements were incorporated into diesel fuel oil to increase their performance. As a result of research of fragments of spent catalysts by the IR methods and an emission spectroscopy it was succeeded to define the possible content of elements, potentially dangerous to the catalyst, in exhaust gases flow (tab.4). Thus, the performed researches showed that the catalysts are subjected to the combined effect of the exhaust gases. According to data of electron microscopy and XPS the noble metal in the initial monodisperse catalysts are in an oxidized state with a uniform distribution of metal particles on the carrier and are characterized by high thermal stability. The main difference between the synthesized catalysts is found at determining time of their warming up prior to reaction (200°C) in a stream of diesel exhaust gas in the mode of a no-load operation (420.0 rev/min). The studied catalysts may be arranged in a row: 0.1 weight of % of Pt (2 min.), % Pd-0.2 (4 min.), % Pd-0.1 (7 min.).

Table 4 – Impurities, potentially dangerous to the used catalysts, which are contained in exhaust gases of the diesel engine

Element	The finding form	Possible quantity, %	Assignment	Total amount of impurities passing through the catalyzate, g
S	SO_2-SO_3	0.04-0.4	impurity in fuel and oils	0.5-5.0
P, Zn	Zn dithiophosphate	0.1-0.2	corrosion inhibitors and antioxidants	0.4-0.6
Ca	sulfonates	0.3	detergents	-
Mg	phenates	0.1	detergents	-

As the result of the tests it was found that the most effective at all engine operating conditions was the catalyst containing oxides of nickel and manganese, activated by 0.1% of Pt. On quality of ecological cleaning of combustion gases the catalyst complies with the environmental standards of Euro-3. The catalytic samples on the basis of Ni and Mn promoted by Pd (0.1%, 0.25%) and Pt (0.1%), provide high degree of transformation CO to CO_2, C_xH_y into CO_2 and H_2O, NO to N_2.

Results of tests of the diesel engine-generator of KamAP (tab.5) equipped with the catalytic neutralizer of fulfilled gases which was elaborated by the authors of this article, show, that application the catalytic neutralizer of the fulfilled gases resulted in decrease in harmful emissions in comparison with the engine without neutralizer: on NO_x-33.0 %, C_xH_y – 82.0 %, CO-98.0 % (2200 rev./min.). On a mode of the minimal idling (800 rev./min.) efficiency of neutralizer has made on NO_x-59.0 %, C_xH_y-86.0 %, CO-99.0 %.

Results of neutralization of toxiferous emissions on the S. Balgimbayevo field are given in tab. 6. Catalytic filters were installed on several furnaces of heating of oil and water on the Southwest Kamyshitovoye field (Kazakhstan): on the PT-3,5 furnace with the forced feed of air and on 4 furnaces PT-16/150 with own pull of air. Decrease in toxiferous emissions on the South-West Kamyshitovoye field on the PT-16/150 furnace after the catalyst amounted to: on CO –100%, on NO -7.7%, on NO_x-7,7%, on SO_2 – 57.1%.

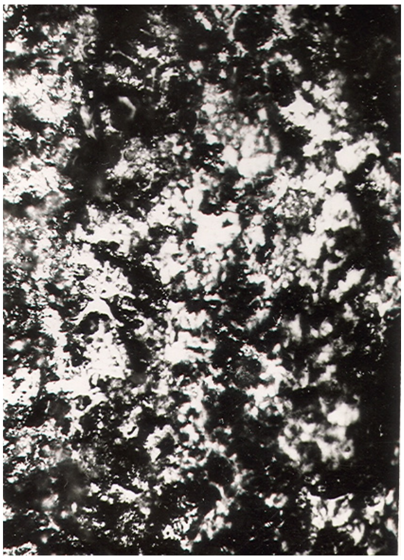
Table 5 – Tests of the full-sized catalysts for neutralization of toxic emissions of engine KamAP

Number of revolutions, rev./min.	CO, ppm			C_xH_y, ppm			NO_x, ppm		
	without neutralizer	with neutralizer	degree of cleaning, %	with out neutralizer	with neutralizer	degree of cleaning, %	without neutralizer	with neutra lizer	degree of cleaning, %
800	123	1.3	99	3182	445	86	128	75.25	59
2200	733	8	98	3728	671	82	118	79.06	33

Table 6 – Test of full-size catalytic neutralizers on furnaces of heating of oil on the "S. Bal-gimbayevo" field

The toxic components	The toxic gases content, ppm		The cleaning efficiency, %
	Initial, without neutralizer	after neutralizer	
CO	1,280.0	5.0	99.6
NO	49.0	39.0	20.4
NO_x	51.0	41.0	19.6

X-ray phase analysis and EM (electron microscope EM-125 K) physical and chemical researches of catalysts show that the prepared oxide catalysts represent spinels with a cubic lattice with $NiMnO_4$ peaks 2Å, 52Å, 148Å, 203Å. There were also revealed low-intensity reflexes of alumina (160Å, 256Å), in the catalysts on the base of manganese are formed the particles which are finely dispersed, uniformly distributed on the surface of the carrier. X-ray analysis showed Pd and Pt scattering spectrum, which indicates a high dispersion of the metal (fig.5). Pt particle sizes are 7-8 nm, Pd-11 nm.



a

b

Figure 6 – The nanosized particles (300, 000 magnification) : a – Pt, b – Pd

Conclusion

Thus, the catalysts supported on metal block carriers for cleaning of exhaust gases of motor transport were developed and tested in the laboratory and in real operating conditions of vehicles of motor transport. Stability of the carrier and the active phase of the catalysts supported on metal blocks to poisoning by water vapor is investigated. At poisoning by water vapor of catalysts promoted with Pt they are activated again under heating at T=300°C under a stream of dry air for 4 hours. In the presence of steams degree of transformation of nitrogen oxide on the catalysts which are not promoted by Pt decreases to zero whereas the catalysts promoted by 0.1% of Pt (wt.) kept higher activity during 50 h of an experiment. The full-size catalysts with various active phase on metal block carriers were tested on natural gases of the stationary diesel generator of brand 5GF-LDE with power of 5 kVA at various loadings. The prepared catalysts at 200°C and above provide high performance in bench tests. The most effective at all engine operating conditions was the catalyst containing oxides of nickel and manganese, activated by 0.1% of Pt. Full-size catalyst samples were tested on truck of KamAP running on diesel fuel. Thanks to the use the catalytic converter exhaust emissions are reduced (in comparison with the engine without catalyst) on NO_x-33.0%, C_xH_y-82%, CO-98% (at 2,200 rev/min). At a minimum idling mode (800 rev/min.) the efficiency of the neutralizer was on: NO_x-59%, C_xH_y-86%, CO-99%. Decrease in toxiferous emissions on the South-West Kamyshitovoye field on the PT-16/150 furnace after the catalyst amounted to: on CO –100%, on NO -7.7%, on NO_x-7,7%, on SO_2 – 57.1%. Decrease in toxiferous emissions on the "S. Balgimbayevo" field: on CO – 99.6%, on NO -20.4 %, on NO_x-19.6 %.

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