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## The Influence of Deposit Control Additives on Nitrogen Oxides Emissions from Spark Ignition Engines (Case Study: Tehran)

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**Abstract:** In the present research, the influence of a deposit control additive on NO<sub>x</sub> emissions from two types of gasoline engine vehicles i.e., Peykan (base on Hillman) and Pride (South Korea Kia motors) was studied. Exhaust NO<sub>x</sub> emissions were measured in two stages, before decarbonization process and after that. Statistical analysis was conducted on the measurement results. Results showed that NO<sub>x</sub> emissions from Peykans increased 0.28% and NO<sub>x</sub> emissions from Pride automobiles decreased 6.18% on average, due to the elimination of engine deposits. The observed variations were not statistically and practically significant. The results indicated that making use of detergent additives is not an effective way to reduce the exhaust NO<sub>x</sub> emissions from gasoline engine vehicles.

**Key words:** Spark ignition engines, deposit control additive, nitrogen oxides emissions, Tehran

### INTRODUCTION

The air pollution is a serious and inevitable problem in large cities. Air pollution is particularly significant for developing countries, where rapid rates of both urbanization and growth in vehicle fleet are expected to be the highest in the world. The population of Tehran (the capital of Iran) has rapidly increased in recent two decades. Amongst several environmental problems in Tehran, air pollution is one of the major concerns. The exhaust emissions from spark ignition engines accounts for a major portion of this problem in Tehran, since the majority of vehicles in Tehran use a spark ignited gasoline engine to provide power and this has become the most frequent form of transportation. The increasingly use of gasoline engine vehicles in Tehran, especially in recent years, has led to deterioration of the quality of air to a level, which ranks Tehran among the most polluted cities in the world. The considerable fraction of passenger car fleet in Tehran is over 20 years old with poor fuel efficiency and lacking catalytic converters. More than 98% of gasoline in Iran is consumed in the transportation sector. Tehran contributes to about one-fourth of the total gasoline consumption in Iran.

Nitrogen oxides are one of the main groups of pollutants in exhaust emissions from spark ignition

engines. Between energy sub-sectors in Iran, the transportation sector contributes to about 64.3% NO<sub>x</sub> emissions (EER, 2004). Nitrogen oxides, in presence of sunlight, combine with hydrocarbons and form photochemical oxidants that do have adverse effects on human health (Wark *et al.*, 1998). Generation of NO<sub>x</sub> is enhanced by high, local peak temperatures and a corresponding excess of air. NO emissions account for approximately 90-98% of all NO<sub>x</sub> emissions during engine operation (Abdel-Rahman, 1998).

Engine deposits derived mainly from the gasoline are usually formed on all internal surface of a spark-ignition engine (Abdel-Rahman, 1998). Deposits normally form in the combustion chambers (piston tops and cylinder heads) of gasoline spark ignition engines (Nelson *et al.*, 2002). It has long been recognized that combustion chamber deposits could adversely affect the operation of spark-ignition engines. Such deposit accumulation can lead to various forms of abnormal combustion. In addition to degrading engine performance, deposit-caused abnormal combustion also impacts engine emissions (Zerda *et al.*, 2001). Interest in combustion chamber deposits and their effects on engine emissions has increased as fuel and additives technology to control deposits in other parts of the engine has matured (Abdel-Rahman, 1998). Emissions of unburned

hydrocarbons and carbon monoxide have been suggested to increase with engine deposit formation, but the effect of CCD on both CO and HC emissions is not clearly established (Kalghatgi, 1995). However, it has been observed in the majority of studies that the accumulation of engine deposits may lead to an increase in NO<sub>x</sub> emissions (Abdel-Rahman, 1998; Zerda *et al.*, 2001; Bower *et al.*, 1993; Studzinski *et al.*, 1993). Formation of NO<sub>x</sub> during the engine cycle (base on Zeldovich, 1946) reaction mechanism) has been shown to have a strong dependence on mean gas temperature in the cylinder, increasing by over 44% with an increase in burned gas temperature from 2000 K to 2050 K. Thus, the increase in gas temperatures due to the insulating and heat-storage effects of the deposits can be expected to increase engine-out NO<sub>x</sub> emissions. Statistically significant increases in tailpipe NO<sub>x</sub> emissions with increasing deposit thickness have been observed experimentally (Bitting *et al.*, 1994). Harpster *et al.* (1995) reported that engine deposit formation and accumulation could increase NO<sub>x</sub> emissions up to 25%, where the observed increase was dependent on the fuel structure. The increase is related to the increase in bulk gas temperature brought about by the combustion chamber deposits. Thus it seems that the removal of engine deposits may leads to reduction in NO<sub>x</sub> emissions.

As SI engine vehicles are the major contributor to Tehran air pollution, controlling techniques and strategies to reduce engine exhaust emissions need to be developed. In line with Iranian department of environment policies to reduce Tehran air pollution, more that 250,000 SI engine vehicles were decarbonized in Tehran. In decarbonization process a mixture of gasoline and additive (with certain proportions) was injected into engine to remove deposits from internal surfaces of engine and fuel system by making a chemical reaction.

One of the main goals of this project was to reduce NO<sub>x</sub> emissions from gasoline engine vehicles. In the present research, the influence of a deposit control additive on NO<sub>x</sub> emissions from Peykan (base on British Hillman) and Pride (base on South Korea Kia motors) vehicles was studied. These are the most frequent cars in Iran (and also in Tehran).

## MATERIALS AND METHODS

Decarbonization project was conducted under supervision of Iranian department of environment from the first of July 2004 to the end of January 2005. Tailpipe emissions were continually measured in parallel with decarbonization operations for seven months. After decarbonization process, vehicles which had no technical problem were selected randomly for emission

measurement. Peykan and Pride are carbureted engine vehicles with no exhaust emission control system, e.g. catalytic converters. During the emission tests, the engines were operated at idle condition. The measurement of exhaust NO<sub>x</sub> emissions was conducted in two stages, before and after decarbonization process, in order to quantify the effect of decarbonization process on NO<sub>x</sub> emissions level. Also considering the advice of solvent manufacturer, the automobiles traveled several kilometers between two tests, in order to provide enough time for reaction fulfillment between the detergent additive and engine deposits.

Power clean solvent manufactured by Power Clean 2000 Inc. was used as detergent additive in this study. This detergent additive has patented technology. Commercial unleaded gasoline was used as base fuel for the preparation of gasoline/Power Clean solvent mixture (solvent to gasoline ratio: 1 to 5) for tested vehicles. Iranian department of environment recommended using a dosing level of 4 ounce of detergent additive for each 4-cylinder vehicles, base on solvent manufacturer recommendation. EVC2000 unit (manufactured by Power Clean 2000 Inc.) injected the mixture of detergent additive/gasoline into engines. The observed effect of Power Clean 2000 solvent on the combustion chamber deposits of a vehicle, before decarbonization process and after that is shown in Fig. 1.

An AVL digas 4000 light analyzer was used to measure the concentrations of NO<sub>x</sub>. The analyzer provided a NO<sub>x</sub> measurement range of 0 to 4000 ppm (10<sup>-4</sup> percent of volume) with a resolution of 1 ppm. The measurement of NO<sub>x</sub> (as NO) was made by electrochemical cell. The sampling duration for each vehicle was about 30 sec. The calibration of the analyzer was performed and certified by the Rizo Engineering Ltd. (manufacturer partner in Iran) once every six months.

Statistical analysis was conducted on the measurement results (exhaust NO<sub>x</sub> concentrations before

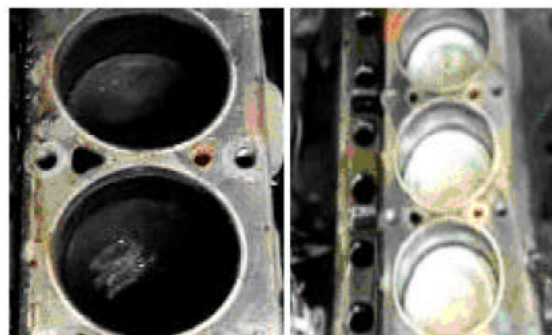


Fig. 1: The influence of detergent additive on combustion chamber deposits

decarbonization process and after that). The measurement results were analyzed by SPSS software. In order to comparing NO<sub>x</sub> concentrations means, before and after decarbonization process, paired sample t-student test was done on measurement results. The statistical significance level is 5%. Outlier data were removed by Box-and-Whisker methods (Mac Berthoues and Brown, 2002; Pezeshk and Izad Doostdar, 2001).

## RESULTS AND DISCUSSION

In the present study, exhaust NO<sub>x</sub> emissions from 192 Peykan and 227 Pride were measured in to stages, before decarbonization process and after that. Surveying the decarbonization process effect on exhaust NO<sub>x</sub> emissions variation was also conducted base on the vehicle model year. Results of NO<sub>x</sub> emission measurements for Peykan vehicles are presented in Table 1. Table 1 also summarizes the statistical analysis results for different model year vehicles. The average change of exhaust NO<sub>x</sub> emissions from Peykan automobiles, affected by decarbonization process is between -13.26 and 15.35% for different model years. The results show that the influence of decarbonization process on exhaust NO<sub>x</sub> emissions from

Peykan vehicles, other than those made in 1998 and 2003 was not statistically significant. The maximum significant reduction in NO<sub>x</sub> emissions from Peykan vehicles was obtained for the model made in 2003 (13.26% decrease). The mean concentrations of exhaust NO<sub>x</sub> emissions from Peykans with different model years were in the range of 42.24 to 74.5 ppm before decarbonization and in the range of 42.92 to 70.4 ppm after that. The average of NO<sub>x</sub> concentrations were increased in almost half of the cases and decreased in the other half of them, however most of the changes were not significant.

The trend in NO<sub>x</sub> emissions from vehicles with different model years and the influence of decarbonization process on tested vehicles are shown in Fig. 2 and 3. It can be shown in Fig. 2 that the exhaust NO<sub>x</sub> emissions from Peykans with different model years are close to each other before and after decarbonization process and there is no considerable difference between them. Peykan vehicles which made in 2002 have got the least amount of exhaust NO<sub>x</sub> emission (42.24 ppm) and Peykans made between 1976 and 1986 have got the most amount of exhaust NO<sub>x</sub> emission (74.5 ppm), among the other models. The emission level of exhaust NO<sub>x</sub> of worn-out Peykan automobiles (with the models made before 1976)

Table 1: The influence of decarbonization process on exhaust NO<sub>x</sub> emissions from peykan vehicles

Model year	No <sub>x</sub> concentration before decarbonization (10 <sup>-4</sup> percent of volume)	No <sub>x</sub> concentration after decarbonization (10 <sup>-4</sup> percent of volume)	Observed difference (%)	SE	p-value
Before 1976	47.61	44.50	6.53	3.30	NS
1976-1986	74.50	70.40	5.50	7.85	NS
1986-1996	71.18	63.64	-10.60	13.26	NS
1996	60.44	63.22	4.60	4.01	NS
1997	57.46	62.46	8.70	5.00	NS
1998	63.80	56.00	-12.23	2.08	*
1999	55.82	57.85	3.64	2.40	NS
2000	59.81	59.96	0.25	4.43	NS
2001	57.41	66.22	15.35	5.27	NS
2002	42.24	42.92	1.61	2.44	NS
2003	54.93	47.64	-13.26	2.91	*

NS: Not Significant (p>0.05), \*: Differences between NO<sub>x</sub> concentrations, before and after decarbonization are significant at p<0.05

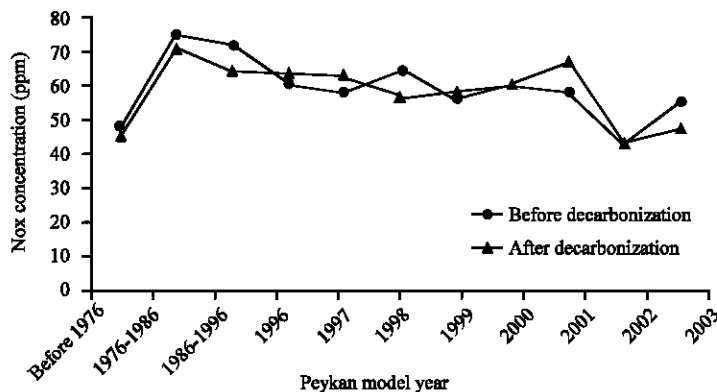


Fig. 2: The exhaust NO<sub>x</sub> emissions from Peykan vehicles with different model years

Table 2: The influence of decarbonization process on exhaust NO<sub>x</sub> emissions from pride vehicles

Model year	No <sub>x</sub> concentration before decarbonization (10 <sup>-4</sup> percent of volume)	No <sub>x</sub> concentration after decarbonization (10 <sup>-4</sup> percent of volume)	Observed difference (%)	SE	p-value
Before 1996	142.83	122.42	-14.29	19.35	NS
1996	134.84	130.37	-3.32	7.61	NS
1997	127.19	136.57	7.38	13.62	NS
1998	135.61	121.56	-10.36	9.87	NS
1999	117.27	101.32	-13.60	9.75	NS
2000	124.12	105.44	-15.05	9.52	NS
2001	124.43	116.91	-6.04	7.39	NS
2002	97.41	93.07	-4.46	4.54	NS
2003	69.06	76.00	10.05	6.96	NS

NS: Not Significant (p>0.05)

Table 3: The influence of decarbonization process on NO<sub>x</sub> emission from all tested vehicles

Vehicle type	No <sub>x</sub> Concentration before decarbonization (10 <sup>-4</sup> percent of volume)	No <sub>x</sub> Concentration after decarbonization (10 <sup>-4</sup> percent of volume)	Observed difference (%)	SE	p-value
Peykan	58.4	58.56	0.28	1.72	NS
Pride	116.75	109.53	-6.18	3.01	*

NS: Not Significant (p>0.05), \*: Differences between NO<sub>x</sub> concentrations, before and after decarbonization are significant at p<0.05

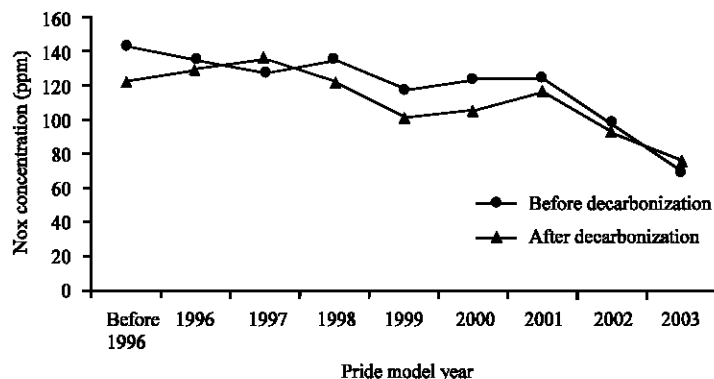


Fig. 3: The exhaust NO<sub>x</sub> emissions from Pride vehicles with different model years

is less than the Peykan automobiles which were made in recent years. The results indicate that the engine deposits do not have considerable role in variation of exhaust NO<sub>x</sub> emissions from Peykan automobiles.

The measurement results are associated with NO<sub>x</sub> emissions before decarbonization process and after that Table 2. The statistical analysis results for Pride automobiles with different model years were also summarized in Table 2. The results show that decarbonization of these automobiles could not considerably affect the emission levels of NO<sub>x</sub> in any of the cases. The mean concentrations of exhaust NO<sub>x</sub> emissions from Pride vehicles with different model years were in the range of 69.06 to 142.83 ppm before decarbonization process and in the range of 76 to 136.57 ppm after that. The average change of exhaust NO<sub>x</sub> emissions from Pride automobiles, due to decarbonization process is between -15.05 and 10.05% for different model years, however these changes were not statistically significant.

A decreasing trend in exhaust NO<sub>x</sub> emission from different model years can be shown in Fig. 3 so that the

Pride automobiles made before 1996 has got the most amount of exhaust NO<sub>x</sub> emission (142.83 ppm) and the ones made in 2003 has got the least amount of exhaust NO<sub>x</sub> release (69.06 ppm). However generally the results of this section indicates that the removal of engine deposits from Pride automobiles like Peykan automobiles does not have the effective role in decrease or increase of exhaust NO<sub>x</sub> emissions from these automobiles.

The statistical analysis of the obtained data for all tested Pride and Peykan automobiles indicates that the exhaust NO<sub>x</sub> emissions from Peykans increased 0.28% and the exhaust NO<sub>x</sub> emissions from Pride automobiles decreased 6.18% on average, due to the elimination of engine deposits. This means that exhaust NO<sub>x</sub> emission level from Peykan automobiles remains almost constant before and after removal of deposits. Additionally, however the 6.18% reduction in exhaust NO<sub>x</sub> emissions from Pride automobiles, affected by the elimination of engine deposits, was statistically significant but as it can be shown in Table 3 this variation is practically negligible. In fact there is no considerable difference between 109.53 and 116.75 ppm. The results also indicate that the

Pride's exhaust NO<sub>x</sub> emission level is double of that of Peykan automobiles. This is probably due to the combustion quality difference in Peykan and Pride engines and higher combustion temperature in Pride automobiles that causes the increase of NO<sub>x</sub> formation and emission.

The results of several studies done in this field imply the availability of relationship between exhaust NO<sub>x</sub> emissions from SI engines and engine deposit formation (Abdel-Rahman, 1998; Bower *et al.*, 1993; Studzinski *et al.*, 1993). Unlike the results of these studies, current research indicates that the engine deposits have no considerable influence on exhaust NO<sub>x</sub> emissions from SI engine automobiles. It is noticed that the exhaust emission measurement tests were conducted at idle condition. Dynamometric tests are recommended to investigate the influence of different driving conditions on the NO<sub>x</sub> emissions from vehicles, before and after decarbonization process.

The technology difference between the tested vehicles in this research and the other studies could affect the influence of deposits on exhaust NO<sub>x</sub> emissions but it seems that the main reason of the differences between results of this research and other studies is that the other vehicle engines were just tested in laboratorial conditions but current study measured the real emissions of NO<sub>x</sub> from on road vehicles. Thus the real effect of engine deposits removal on exhaust NO<sub>x</sub> emissions from SI engine vehicles observed in this study.

### CONCLUSION

In the present study, the influence of engine deposit removal by decarbonization process on the exhaust NO<sub>x</sub> emissions was studied. The measurement results and data analysis indicates that the elimination of deposits from Peykan and Pride engines does not have any considerable effect on the exhaust NO<sub>x</sub> emissions. This study also shows that the model year of Pride and Peykan automobiles does not have any remarkable role on the exhaust NO<sub>x</sub> emissions. In the other word, the general result of this research was almost independent from the model year of tested vehicles. Finally the present research shows that making use of detergent additives is not an effective way to reduce the exhaust NO<sub>x</sub> emissions from gasoline engine vehicles.

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