# The Multifunctional Automobile Gasoline Additive on the Basis of Amino-Aromatic Hydrocarbons and Oxygen-Containing Compounds

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## Abstract

Octane improvement can be attained by two ways. They are increasing the high-octane oil fraction output and using the alternative antiknock additive. The first method is reasonable for countries with developed oil refining system, which possess sufficient capacities for catalytic cracking, isomerization and alkylation. At this time the second version is more suitable to Kazakhstan's oils. The additive is represented in the paper; this additive allows to increase antiknock properties (octane number) and to decrease harmful component content in exhaust gases, tar deposit on engine feed system as well as to extend the term of service of catalysts for exhaust gas purification.

Regulation the high knock characteristic of gasoline is one of requirements to motor fuel producers. It is attained by up-to-date technological processes using with minimal hydrocarbon material losses associated with it's conversion into less valuable side products.

Aromatic amines are ammonia derivatives like fatty amines. An amine group can be bonded with a nuclear directly or be in a lateral chain. Like in aliphatic series aromatic amines can be primary, secondary and tertiary ones. Depending on radicals (aromatic only or aromatic and aliphatic) bonded with an atom of nitrogen, pure aromatic and fatty aromatic amines are distinguished. N-methylaniline (monomethylaniline, extraline) refers to the substituted arylamine class. High-antiknock additive MMA and thereupon basis additives are used at petroleum refining enterprises to adjust gasoline octane number in production of any mark gasoline. MMA conforms to up-to-date European standards in physical-chemical and operational properties. MMA is several times more cost-efficient than MTBE. To increase octane number from 76 till 92, 2.5% MMA is required.

## Introduction

Regulation the high knock characteristic of gasoline is one of requirements to motor fuel producers. It is attained by up-to-date technological processes using with minimal hydrocarbon material losses associated with it's conversion into less valuable side products.

Native technologies of gasoline production differ significantly from abroad ones. Gasoline fractions of catalytic reforming and straight distillation dominate in our Kazakhstan's gasoline. The low content of gasoline fractions of catalytic cracking and insignificant content of alkylate and isomerization product is typical to it.

Octane improvement can be attained by two ways. They are increasing the high-octane oil fraction output and using the alternative antiknock additive. The first method is reasonable for countries with developed oil refining system, which possess sufficient capacities for catalytic cracking, isomerization and alkylation. At this time the second version is more suitable to Kazakhstan's oils.

Antiknock additive list is largish. It can be represented through three classes: aromatic amines, metal-containing and oxygen-containing compounds. Metal-containing compounds are widely spread neither in our country nor abroad. Among aromatic amines N-methylaniline (monomethyl aniline) and thereupon basis compositions are only used; these compounds have a certain interest not only in Kazakhstan. These

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antiknock additive classes can be used both as individually and as each other combination. Taking into account severization to waste gas toxicity abatement, the additives containing alcohols, ethers and other class compounds increasing fuel combustion efficiency are in great demand [1].

Thus among aromatic amines N-methylaniline and diphenylamine are of greatest interest for petroleum refining industry.

According to antiknock ability amines range in decreasing order by following manner [2]:

*aromatic>heterocyclic>aliphatic>cyclo-aliphatic*

In this quality N-methylaniline ($C_6H_5NHCH_3$) is one of most effective amines used for gasoline.

## Experimental

### *Chemicals*

Aromatic amines are ammonia derivatives like fatty amines. An amine group can be bonded with a nuclear directly or be in a lateral chain. Like in aliphatic series aromatic amines can be primary, secondary and tertiary ones. Depending on radicals (aromatic only or aromatic and aliphatic) bonded with an atom of nitrogen, pure aromatic and fatty aromatic amines are distinguished.

Among aromatic amines the next compounds (besides N-methylaniline) have best antiknock properties: xylidine, cumenylamine and diphenylamine. Comparative efficiency of aniline homologous compound is given [3] in the Table 1.

**Table 1**
Comparative efficiency of aniline homologous compound

| Aniline homologous compound | Formula | Relative efficiency, % |
|---|---|---|
| Aniline | $C_6H_5NH_2$ | 100 |
| Toluidine | $CH_3C_6H_4NH_2$ | 122 |
| *m* - xylidine | $(CH_3)_2C_6H_3NH_2$ | 140 |
| Cumenylamine | $(CH_3)_3C_6H_2NH_2$ | 151 |
| Ethyl-aminobenzene | $C_2H_5C_6H_4NH_2$ | 114 |
| Monomethyl aniline | $C_6H_5NHCH_3$ | 140 |
| Diphenylamine | $C_6H_5NHC_6H_5$ | 150 |

### *Instruments*

To perform the experiment the next chemicals are required: aniline, methanol, catalyst (for N-methylaniline preparation); methylthree-butyl ether (MTBE), diphenylamine, hydrocarbon fraction (200 °C), NaOH, $H_2SO_4$.

Instruments: electric heater, water bath, flask, thermometer, indicator paper, octane-meter.

## Synthesis

### *N-methylaniline synthesis*

N-methylaniline (monomethylaniline, extraline) refers to the substituted arylamine class. High-antiknock additive MMA and thereupon basis additives are used at petroleum refining enterprises to adjust gasoline octane number in production of any mark gasoline [4].

MMA conforms to up-to-date European standards in physical-chemical and operational properties. MMA is several times more cost-efficient than MTBE. To increase octane number from 76 till 92, 2.5% MMA is required.

Taking into account N-methylaniline importance for petroleum refining industry, the continuous production of this product has been developed and implemented in OAO “Volzhsky orgsynthesis” in 1995, and above mentioned disadvantages have been eliminated in this production. The process is based on vapour-phase aniline N-hydroalkylation in the presence of hydrogen and hydrating-dehydrating catalyst [5].

Along with N-methylaniline the side product N,N-dimethylaniline is formed in trace amounts in the given process conditions according to the following reaction equation:

$$C_6H_5NH\text{-}CH_3 + CH_3OH \rightarrow C_6H_5N(CH_3)_2 + H_2O$$

The reaction of product gumming:

$$2\ C_6H_5N(CH_3)_2 + CH_2O \rightarrow [C_6H_4N(CH_3)_2]_2 + H_2O$$

Methanol decomposition:

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$$

In specified conditions the catalyst operated continuously without regeneration during 2 years, herewith 90.0-99.0% aniline conversion per pass id reached, and N-methylaniline output is 95.0-98.5% of converted aniline. A catalyzate obtained in the process, contains N-methylaniline, water, non-reacted aniline and methanol as well as small amount of N,N-dimethylaniline. Commercial N-methylaniline is separated out of a catalyzate by the method of continuous rectification [6].

A large number of projects is devoted to composite antiknock agents, containing oxygenates, ferrum and manganese compounds and amines in various combinations. It allows to summarize an antiknock effect of all additive components, and in some cases to reach a synergetic effect. Wide experience of such developments in Russia speaks for functional compatibility of additive components [7, 8] (Table 2).

We add diphenylamine, methanol, MTBE, hydrocarbon fraction and ethanol to the obtained product

**Table 2**
Functional compatibility of additive components

| Compounds | Ferrocene | MCTM | Amines | Oxygenates |
|---|---|---|---|---|
| Ferrocene | | - | + | - |
| MCTM | - | | + | 0 |
| Amines | + | + | | + |
| Oxygenates | - | 0 | + | |

Notations: MCTM - methylcyclopentadieniltricarbonylmanganese; + - alcohol; - - antagonism; 0 – simple summation.

## Results and Discussion

We have developed the additive based on noncritical products of industrial production, with high antiknock properties and providing gasoline improved stability at low temperature and storage.

The proposed additive contains additionally hydrocarbon fraction 60-200 °C. Matching ratio of components in it provides improved stabilizing properties. An antioxidant and a detergent additive injected into additive composition provide improved operative and environmental characteristics to gasoline.

Testing result (Table 3) have confirmed that only joint content of monomethylaniline, ethanol, acetaldehyde and hydrocarbon fraction in the additive composition provides it's high antiknock properties, improved stability at low temperatures and high operational characteristics.

**Table 3**
Additive composition and testing results

| Components, % | Additive samples | | | | | |
|---|---|---|---|---|---|---|
| N-methylaniline and diphenylamine mix | 9 | 12 | 15 | 18 | 21 | 24 |
| Methanol | 15 | 17.5 | 20 | 22.5 | 25 | 27.5 |
| MTBE | 20 | 20 | 20 | 20 | 20 | 20 |
| Acetaldehyde | 5 | 5 | 5 | 5 | 5 | 5 |
| Hydrocarbon fraction 60-200°C | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 | 2.5 |
| Detergent additive AMDOR | 3 | 3 | 3 | 3 | 3 | 3 |
| Ethanol | up to 100 | up to 100 | up to 100 | up to 100 | up to 100 | up to 100 |
| Additive petrol | | | | | | |
| Addittive concentration, % (mass) | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
| Chemical stability: Cumulative content of oxidation products, mg/cc | 31.8 | 31.6 | 31.6 | 33.4 | 34.2 | 32.6 |
| Corrosion activity (steel 10), $g/m^2$ | 0.5 | 0.5 | 1.2 | 1.5 | 0.8 | 0.4 |
| Detergency, $K_{wa}$ | 82 | 84 | 76 | 75 | 82 | 84 |
| Octane number increase (motor method): | | | | | | |
| standard fuel | 9.7 | 9.7 | 8.9 | 10 | 9.8 | 10 |
| straight-run gasoline | 11 | 12.2 | 10.2 | 11.3 | 11.2 | 11.5 |

When multifunctional additive using, one can improve application properties of standard fuel. Builders in ethanol based additive allow to improve it's protective, ecological, detergent properties etc. Besides that, ethanol based additives promote to increase the commercial gasoline octane number.

Proposed additive allows to increase the production of premium automobile gasoline, which will provide the purity of engine fuel system under it's stretching.

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