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(57) Abstract: The invention refers to an additive for the gasoline. The additive according to the invention is an admixture of aromatic amines, preferably N-methylaniline and organometallic compounds containing manganese, preferably methylcyclopentadienyl manganese (II) tricarbonyl and optionally an organic compound containing oxygen, such as an ether, an ester or an alcohol.



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SYNERGISTIC OCTANE BOOSTER ADDITIVES CONTAINING AROMATICS AMINES AND MANGANESE AND GASOLINE RESULTED FROM THEIR USAGE

5 The present invention refers to a process for obtaining octane-booster additives whose compositions comprise at least an aromatic amine, such as N-methylaniline; a manganese compound such as bis-(dicyclopentadienyl)manganese, methylcyclopentadienyl manganese tricarbonyl or manganese carbonyl, and optionally an oxygenated compound belonging to the class of ethers or alcohols and also to the automotive gasoline obtained
10 from basic gasoline and the above mentioned additives.

For a correct operation, spark-ignition engines require gasoline having high octane numbers, Research Octane Number (RON) > 95 and Motor Octane Number (MON) > 85. The terms RON and MON are specific to the measurement procedure. Further, in USA and Canada the octane number AKI (average knocking index) representing the mean
15 $(RON + MON)/2$ is used. The gasoline is manufactured by processing the crude oil by distillation, cracking, isomerization and alkylation. Since in most cases the manufacture of gasoline having RON =95 implies increased costs and simultaneously decreased efficiency, by admixing gasoline manufactured by different technological processes, the so-called basic gasoline having generally RON<95 is obtained. Furthermore, according to
20 the Standard EN 228:2004 applied in EU, when referring to the compositions and physical characteristics, the compositions of the gasoline approved for the use in the automotive engines imply drastic restrictions: S< 10 mg/kg; aromatic hydrocarbons < 35% vol/vol. (content of benzene: < 1% vol/vol; olefin < 18% vol/vol, final boiling point 210°C, % vol/vol distillation residue < 2%, density at 15°C: 720-775 kg / m³ etc., and in the future, in order
25 to reduce noxious emissions, new restrictions on the content of aromatic materials will be imposed. Because of all these restrictions, the oil processing becomes more complicated and new technical problems arise.

For obtaining gasoline having high octane number, there are used processing fractions containing isoparaffins, cycloparaffins, and aromatic materials, these classes of
30 hydrocarbons being characterized by high octane numbers. The octane number of gasoline represents its knocking resistance. Due to the influence of the temperature of the flame front, the vapour of the hydrocarbon molecules having long straight chain produce high quantities of reactive hydrocarbon radicals. They react with the oxygen of the ignition air and keep the formation of the OH* and O* radicals. These radicals propagate the
35 knock by generating radical branched chains. The branched molecules and those bond to the aromatic or saturated cycles are more resistant to the effect of the temperature this explaining the high octane numbers. The increase of the octane number of the basic

gasoline to a value required by the optimal operation of the spark-ignition engines is carried out by using the octane- booster additives. The radicals resulted from the octane-booster additives or even the additives themselves interfere with the radicals generating the knock. Generally, the oxygenated additives produce a local decrease of the temperature, deactivating the radical branched chains. The additives containing metals react with the OH* and O* radicals splitting the propagation branched chains.

The first octane-booster additives used on a large scale were lead tertalkyls which, due to their toxicity, are now prohibited, the lead content in the current gasoline being limited to 5 mg/l. Currently, organometallic compounds containing iron, especially in form of ferrocene, GB226731; US4139349; WO 0116257, containing manganese especially in form of methylpentadienyl manganese(II) tricarbonyl (MMT): US4139349; EP0466511; EP0476197. It was also reported the possibility to use organometallic compounds containing cerium (IV), especially salts with 2,2,6,6-tetramethyl-3,5-heptadione: US3794473; US 4036605 or containing alkaline metals: RU2203927; RU2152981; US3770397. Octane-booster additives containing organometallics have as a main advantage that, at very low concentrations 10-100 mg metal/L, they increase the octane number of the basic gasoline, thus being the cheapest technical solution. The main drawbacks of using organometallic compounds are correlated to the effect of the formation of the metallic oxides onto the equipments of the engine. Thus, the iron oxides have an abrasive effect on the valves of the engine and on the sparking plugs, where, by depositing, they alter the dielectric characteristics. When MMT is used at a concentration of 9-12 mg/L Mn it protects the valves of the engine. Both the iron and manganese oxides alter the operation of the exhaust gas catalytic converter. For this reason the use of manganese with a concentration of maximum 18 mg/L is preferred. For its use at reasonable concentrations, it does not cause negative effects on the noxious gases emissions.

Currently, the ethers of tert-butanol with low aliphatic alcohols are used in large amount as octane-booster additives, the most known being tert-butyl methyl ether (MTBE) and low aliphatic alcohols: Mohammad Ashraf Sli, Halim Hamid, Mohammad Ashraf Ali in "Handbook of MTBE and Other Gasoline Oxygenates" Printed in USA, Marcel Dekker Inc, New York. Basel; 1979; US4468233; US5752992. These additives are generically called oxygenated additives. It is also cited the use of the ethers of the phenols with low alcohols RU2005138060. The main drawback resulted from the use of these additives is the necessity of using high levels. For example, a concentration of 1% wt. MTBE in gasoline increases RON with 0,2-0,3 units, depending on the type of gasoline. The presence of the oxygenated additives results also in the increase of the volatile carbonyl compounds emission in the exhaust gases. In the case of the alcohols, another drawback is the

increase of the corrosion. Therefore, according to the Standard EN 228:2004 applicable in EU, the presence of oxygenated additives in gasoline is restricted to 2,8% wt. oxygen.

Other octane-booster additives industrially used are aromatic amines, especially N-methylaniline: GB252019; GB334181A; GB530597; FR1255840; RU2184767; US2819953; US5470358; EP0235280; WO2008076759. The aromatic amines are 4-15 times more efficient than the oxygenated additives, however their drawback is their price and sometimes the high toxicity (aniline and o-toluidine).

Among the octane-booster additives having high efficiency it can be listed: aminofulvenes: US5118325; aminophenols: WO2007105982; WO2007117176; colouring agents and other structures having extended molecular orbitals: WO2006076020; ortho-azidophenol; ortho-azidoaniline: US4280458. Generally, it is difficult to prepare these compounds which further have prohibitive prices.

The present invention provides several multi-compound compositions which combine the characteristics of several octane-booster additives so that by synergistic interactions the maximum effects can be realized. There are several patents referring to multi-compounds systems of octane-booster additives which claim the synergistic effects, but only in few cases the shown data resist to an objective analysis of the results, considering the definition of the synergism phenomena. The synergistic effect ΔS_x occurs when, in the same gasoline, a series of components $A_1; A_2; \dots A_n$, each one with an individual concentration $c_1; c_2; \dots c_n$ individually induces an increase of the octane number $\Delta[X]_1; \Delta[X]_2; \dots \Delta[X]_i; \dots \Delta[X]_n$, where $[X]$ can be RON; MON; AKI, and the mixture of the compounds $A_1; A_2; \dots A_n$, each one with the same concentration $c_1; c_2; \dots c_n$, in the same gasoline as in the case of their individual participation, has as result a joint increase of the octane number $\Delta[X]$ so that:

$$\Delta[X] > \sum \Delta[X_i];$$

$$\Delta S_x = \Delta[X] - \sum \Delta[X_i] \text{ respectively}$$

With respect to the multi-component octane-booster additives there are several references in the prior art.

Thus, although the patent US4139349 claims the synergetic effects of the mixtures MMT – ferrocene, in all shown cases $\Delta S_{RON} \leq 0$; being in the range from 0 to -1,5.

The patent application WO2005087901 claims several multi-compound systems containing Fe, Mn, K, Ca, Mn organometallic compounds and aromatic amines (aniline, N-methylaniline, ortho-toluidine și para-toluidine). When the shown data allow a calculation of the interactions Fe-K-N-methyl aniline, the effects are antagonistic. In the

case of a gasoline initially having RON=95,0 and MON=83,9, for the additive compositions: Fe 12g/L; K 4,5ppm, it was obtained $\Delta S_{RON} = -0,7$; $\Delta S_{MON} = -1,6$; for Fe 12g/L; N-methyl aniline 0,3% vol/vol. it was obtained $\Delta S_{RON} = -0,3$; $\Delta S_{MON} = 1,0$; for Fe 12g/L; K 4,5ppm; N-methyl aniline 0,3% vol/vol. it was obtained $\Delta S_{RON} = -0,2$; $\Delta S_{MON} = -0,8$. In the case of the compositions 12 -18 g/L Mn; 0 – 4,5 ppm K si 0 – 0,3% vol/vol N-methyl aniline, although the data are not sufficient for an accurate calculation, it can however be estimated that the effects are antagonistic.

The patent RU2235117 shows the ferrocene – alcohols (esters) – aromatic amines interactions. The level of Fe is very high (40-62mg/kg), but comparing with the individual activity of the components, it can be estimated that the presence of iron results in an antagonism.

The patent RU2110561 reports a detailed study referring to the aromatic amines (NMA, xilidine) – MTBE – additives containing iron (α – hidroxy propyl ferrocene; ferrocene) interactions, but the interpretation of the shown data does not allow to establish the nature of the interactions between the components.

The patent RU2117691 claims the binary additives Mn (MMT) – xilidine, the manganese concentrations being much above the admitted limits; 45 – 136 mg/kg, and the interactions effects certainly are antagonistic.

The patent RU2129141 shows different compositions of an tri-component additive N-methyl aniline – ethanol - additives containing iron (ferrocene and α – hidroxy-isopropyl ferrocene). The composition of the additive 5-10% wt N-methyl aniline, Fe 150 – 145,5 mg/kg; ethanol about up to 100%, was dosed 5% wt. into a synthetic gasoline 70% isooctane and 30% n-heptane rendering obvious certain synergetic effects which can be deduced by the results extrapolating.

The patent FR1255840 claims a very strong synergistic effect of the N-methyl aniline (NMA) and MMT added into a gasoline containing 0,18% Pb (as lead tetraethyl). Thus, $[RON]=109,5$ is obtained by adding NMA 0,036 % wt. This means an exceptional contribution of NMA, corresponding to an individual octane number in admixture of $[RON]_{A0}=98,28$. Further adding 0,36 % Mn as MMT a further exceptional increase of $\Delta[RON]=4,5$ occurs. In the absence of NMA the contribution of MMT at the same concentration is only $\Delta[RON]=2,7$.

Other obvious synergism examples between lead tetraethyl and tert-butyl pivalate or Ce(IV) β -diketonate and free β -diketone are shown in the patents FR2050841 and US4211535 respectively. However, the most surprising effect is claimed by the patent US4690687 where the effect of Mn added in gasoline as MMT is significantly intensified by the presence of β -diketones.

The main drawbacks of the different types of the octane-booster additives and the previous shown multi-component systems thereof are the following:

The organometallic octane – booster additives, especially those having high concentrations, alter the different parts of the engine; valves, ignition plugs, catalytic converter and can pollute the environment.

The octane – booster additives belonging to the oxygenated compounds class requires high concentrations into the gasoline, usually 5 -16% and, while increasing their concentrations, the the emission of volatile organic compounds and nitric oxides in the exhaust gases increase.

The octane – booster additives belonging to the aromatic amines class have the drawback of a high cost, and at high concentrations, they can cause the significant increase of the nitric oxides emission in the exhaust gases.

The technical problem solved by the present invention is the preparation of the multi-component octane – booster additives having high efficiency, based on the synergistic interaction of the organometallic compounds containing manganese, preferably as MMT with aromatic amines or mixtures of aromatic amines and oxygenated compounds, the ratio manganese / amines being in a well defined concentration range. The additive dosing is ground on the author's find that for weight ratios of >0-25 mg Mn/g aromatic amine, significant synergistic and demonstrable effects occur, their maximum intensity occurring in the composition range 0,5 – 1,0 mg Mn /g aromatic amine.

The characteristics of the reagents used for formulating the octane-booster additives used by the invention are shown in **Table 1**.

Table 1.

<i>Reagent</i>	<i>CAS#</i>	<i>appearance</i>	<i>purity</i> %	<i>density</i> 20°C; kg/m ³	<i>melt</i> point C	<i>boiling</i> point C
MMT	12108-13-3	liquid	97	1388	1.5	233
N-methyl aniline	100-61-8	liquid	98	989	-57	194-197
N,N-dimethyl aniline	121-69-7	liquid	99	956	2	193
m-toluidine	108-44-1	liquid	99	992	-32 la -30	203-204
p-toluidine	106-49-0	cryst.	>99	973	42-44	199-202
3,5-dimethyl aniline	108-69-0	liquid	>97	971	9-11	220-221
orto-toluidine	95-53-4	liquid	99	1004	-24	199-200
N,N-dimethyl-1,4- phenylene diamine	99-98-9	solid	99	1030	34-36	262

MTBE	1634-04-4	liquid	99	742	-109	55-56
Ethanol	64-17-5	liquid	96	789	-130	78
anhydrous						
denaturated						

The gasoline used for experiments was refinery blending type whose characteristics are shown in **Table 2**

5 **Table 2.**

Characteristic	UM	Value	Analysis standard
density 15C	kg/m ³	732,0	SR EN ISO 3675:03
RON		91,6	SR EN ISO 5164:06
MON		80,8	SR EN ISO 5183:06
olefine	% vol/vol	16,9	SR 1347:02
aromatics	% vol/vol	33,2	SR EN 14517:05
sulfur content	mg/kg	45,0	SR EN ISO 20846:04
evaporation at 100 ⁰ C	% vol/vol	59,2	SR EN ISO 3405:03
final boiling point	C	202,0	SR EN ISO 3405:03
distillation residue	% vol/vol	1,1	SR EN ISO 3405:03
gums	mg/100mL	1,2	SR EN ISO 6246:00

Besides the addition of the synergistic octane-booster additives, the gasoline can be further added with deactivating metals, preferably N,N-disalicylidene-1,2-diaminopropane [CAS 94-91-7] and antioxidants belonging to the class of sterically hindered phenols, preferably 2,6-di-tert-butyl-p-cresol [CAS 128-37-0] in order to prevent the gums formation phenomena and the oxidation, processes catalyzed by the metals.

The main advantages of the present invention are as follows:

- 15 a. the optimization of the consumption of the octane – booster additives in the composition resulting to a reduction of 5 -25% of the consumption, for the same feats comparing with the individually used components.
- b. It decreases with 7 -22% the cost of the gasoline additives
- 20 c. according to the invention, the concentration of the manganese in the gasoline is between 4 and 9 mg/L, thus eliminating the negative effects of the metals presence.

Further, 5 examples are shown.

Example 1: Into the gasoline having the composition of **table 2** with MMT is then added, at different concentrations, N-methyl aniline and finally mixtures of N-methyl aniline and MMT, followed by the measuring of the octane number according to the Standards SR EN ISO 5164:06; SR EN ISO 5183:06. The results of the individually adding of N-methyl aniline and MMT are shown in the **tables 3 and 4** (Δ RON; Δ MON shows the increase of the octane number after adding the additives).

Table 3.

N-methyl aniline % wt	0,0	0,5	1,0	1,5	2,0	2,5
RON	91,6	92,5	93,5	94,4	95,2	95,8
Δ RON	0	0,9	1,9	2,8	3,6	4,2

Table 4.

Mn mg/kg	0	3	6	9	12	15	21
RON	91,6	91,9	92,1	92,4	92,5	92,6	93,0
Δ RON	0	0,3	0,5	0,8	0,9	1	1,4

Further, into the gasoline having the composition of **table 2** are added different admixtures of N-methyl aniline (NMA) and MMT, than measuring the octane numbers according to the standards SR EN ISO 5164:06; SR EN ISO 5183:06 and the results are shown in **table 5**.

Table 5.

Mn mg/kg	0	3	6	9	12	15	18	21	24	30	42
	N-methyl aniline 1% wt										
RON	93,5	93,9	94,5	94,9	95	94,8		95,1			
Δ RON	1,9	2,3	2,9	3,3	3,4	3,2		3,5			
$\Sigma(\Delta\text{RON}_{\text{Mn}} + \Delta\text{RON}_{\text{NMA}})^*$	1,9	2,2	2,4	2,7	2,8	2,9		3,3			
ΔS_{RON}	0,0	0,1	0,5	0,6	0,6	0,3		0,2			
Mn/NMA mg/g	0	0,30	0,60	0,90	0,12	0,15		0,21			
	N-methyl aniline 2% wt.										
RON	95,2	95,5	96	96,5			97		96,8	97	97,1
Δ RON	3,6	3,9	4,4	4,9			5,4		5,2	5,4	5,5
$\Sigma(\Delta\text{RON}_{\text{Mn}} + \Delta\text{RON}_{\text{NMA}})^*$	3,6	4,1	4,4	4,5			5		5,1	5,3	5,7
ΔS_{RON}	0,0	-0,2	0	0,4			0,4		0,1	0,1	-0,2
Mn/NMA mg/g	0	0,30	0,45	0,60			0,90		0,12	0,15	0,21

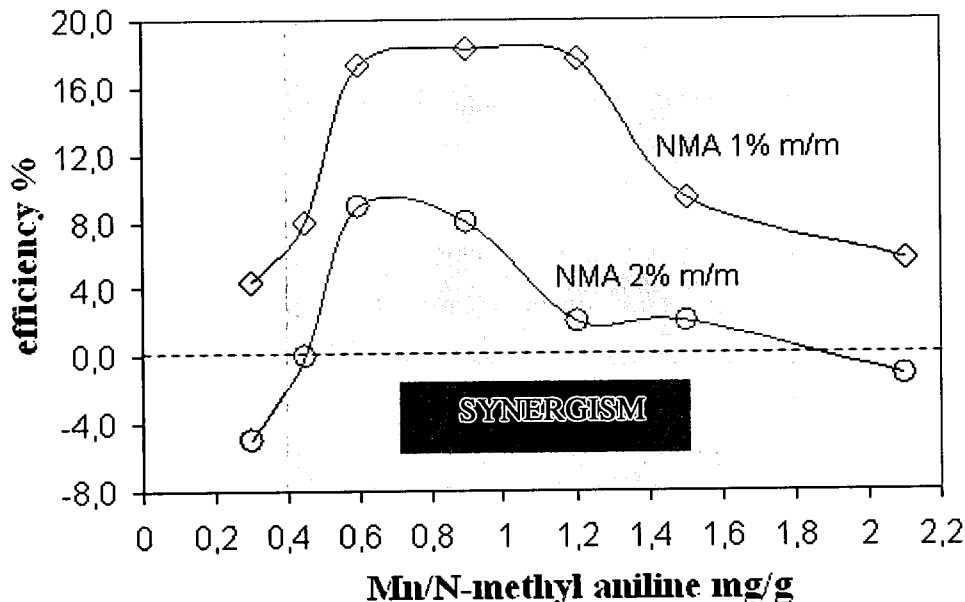
* The contribution of the individual effects

The data interpretation renders obvious the existence of the synergistic interactions. The range of synergism is maximum in the ratios range Mn/NMA 0,6 – 1 mg/kg N-methyl aniline. This range is suggestively shown in **figure 1**, where the percentage increase of the synergistic additive efficiency ΔE is shown comparing with the individual contribution of NMA and MMT, depending on the ratio Mn/ NMA expressed as mg/kg:

$$\Delta E\% = \Delta S_{RON} / \Sigma(\Delta RON_{Mn} + \Delta RON_{NMA}) \times 100$$

The synergistic effect decreases while increasing the concentration of N-methyl aniline. When the concentration of N-methyl aniline is 1% wt., the synergism area is comprised between >0 and >2,2 mg Mn/g N-methyl aniline, while for a concentration of 2% wt. N-methyl aniline, the synergism area is diminished to the range 0,4 - 1,8 mg Mn/g N-methyl aniline, and its intensity is reduced to a half. For uses, the preferred range of the synergistic additives compositions is 0,5 – 1,0 mg Mn/g N-methyl aniline, range in which the synergistic effect intensity is maximum.

Figure 1



Example 2: 97g of N-methyl aniline was admixed to homogenization with 3g of N,N-dimethyl aniline, resulting 100g solution containing 97% wt. N-methyl aniline (NMA) and 3% wt. N,N-dimethyl aniline (NNDMA). 0,52 g MMT was admixed with 9,48g solution 97% wt. aniline and 3% wt. N,N-dimethyl aniline previously prepared, resulting a 13,16 mg/g Mn solution. 2,5 g of solution containing 13,16 mg/g Mn was admixed with 47,5g of

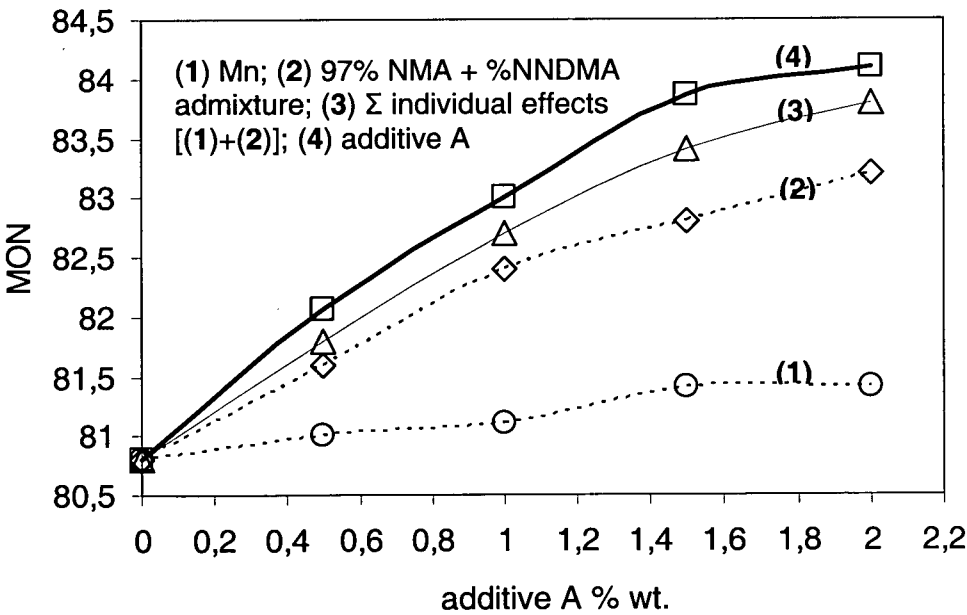
a 97% wt NMA and 3% m/m NNDMA solution resulting a synergistic multi-component octane-booster additive composition containing 0,65 mg Mn/kg, further named additive A. In a next step, to the gasoline whose composition is shown in **table 2**, the solution containing NMA – NNDMA and the additive A at different concentrations were added, measuring the octane numbers according to the Standards mentioned in **example 1**. The comparative results are shown in table 6.

Table 6. Comparison between the efficiency as octane-booster additive of the 97% NMA – 3% NNDMA solution soluției and the additive A

	Concentration % wt.				
	97% NMA – 3% NNDMA Solution				
	0	0,5	1	1,5	2
ΔRON	0	1,2	2,3	3,3	3,9
ΔMON	0	0,8	1,6	2,0	2,4
	Additive A (97% NMA – 3% N,NNDMA + 0,65mg Mn/kg Solution)				
ΔRON	0	1,9	3,3	4,7	5,3
ΔMON	0	1,3	2,3	3,1	3,3

The interpretation of the data of **table 6** and their graphical representation in **figure 2**. obviously show the synergism phenomena.

Figure 2



Example 3: Following the procedure of **example 2** the admixtures I – IX having octane – booster properties and representing the comparison standard and the multi-component synergistic additives I-Mn – IX-Mn having the content of Mn within the synergism range of 0,6 – 1 mgMn/g were prepared. For the additives VII-Mn și IX-Mn, the Mn concentrations were calculated so they be within the range 0,6 – 1 mg Mn/g N-methyl aniline. All these compositions are shown in **table 7**. The additives prepared in this way were dosed up into the basic gasoline having the composition of **table 2** and the octane numbers were measured according to the Standards mentioned in **example 1**; the test results are shown in **table 8**.

Table 7

Name	Composition % wt.	Synergistic additive	
		Name	Mn mg/g
I	N-methyl aniline 97 – anisole 3	I-Mn	0,90
II	N- methyl aniline 50 – p-toluidine 50	II-Mn	0,90
III	N- methyl aniline 75 – m-toluidine 25	III-Mn	0,75
IV	N- methyl aniline 80 - N,N-dimethyl-1,4-phenylenediamine 20	IV-Mn	0,75
V	3,5 – dimethyl aniline – anisole 3	V-Mn	0,80
VI	N- methyl aniline 70 – ethanol ⁽¹⁾ 30	VI-Mn	0,80
VII	N- methyl aniline 30 – ethanol 70	VII-Mn	0,25 ⁽²⁾
VIII	N- methyl aniline 80 – MTBE 20	VIII-Mn	0,80
IX	N- methyl aniline 20 – MTBE 80	IX-Mn	0,15 ⁽³⁾

⁽¹⁾ anhydrous denaturated ethanol with 4,2% isopropanol

⁽²⁾ 8,3 mg Mn/ g N- methyl aniline

⁽³⁾ 7,5 mg Mn/ g N- methyl aniline

Table 8

Dose % wt	Standard additive	Δ RON	Δ MON	Synergistic additive	Δ RON	Δ MON	ΔS_{RON}	ΔS_{MON}
1,0	I	2,2	1,7	I-Mn	3,5	2,5	0,4	0,3
1,0	II	2,3	1,8	II-Mn	3,6	2,8	0,4	0,5
0,5	III	1,2		III-Mn	1,9		0,3	
0,5	IV	1,7	1,0	IV - Mn	2,5	1,5	0,4	0,2
1,0	V	1,8		V-Mn	2,9		0,3	
1,5	VI	2,3	1,2	VI-Mn	3,5	1,7	0,3	0,0
3,5	VII	2,7	1,5	VII-Mn	3,9	2,3	0,4	0,3
1,0	VIII	2,0		VIII-Mn	3,0		0,2	
5,0	IX	2,7		IX-Mn	3,9		0,4	

Example 4: 1kg of multi-component synergistic additive was prepared by admixing and homogenizing 929g N-methyl aniline; 29,7g N,N-dimethyl aniline; 29,7g anisole; 3,6 g MMT; 4g N,N-disalicylidene-1,2-diaminopropane [CAS 94-91-7]; 4g 2,6-di-tert-butyl-p-cresol [CAS 128-37-0]. The resulted amount of multi-component synergistic additive was admixed and homogenized with 99kg gasoline having the composition of **table 2**, resulting 100 kg of gasoline RON 95, whose octane numbers were measured according to the Standards mentioned in **example 1**; the results are shown in **table 9**.

10

Table 9.

Characteristic	Unit	Value	Standard for analysis
density 15C	kg/m ³	734,2	SR EN ISO 3675:03
RON		95,2	SR EN ISO 5164:06
MON		83,7	SR EN ISO 5183:06
final boiling point	C	202,0	SR EN ISO 3405:03
distillation residue	% v/v	1,10	SR EN ISO 3405:03
gums	mg/100mL	2,5	SR EN ISO 6246:00
manganese	mg/L	6,5	SR EN 14517:05

Example 5: 6,5kg of multi-component synergistic additive were prepared by admixing and homogenizing 1891g N-methyl aniline; 58,5g N,N-dimethyl aniline; 4500g anhydrous denaturated ethanol; 3,8 g MMT; 4g N,N-disalicylidene-1,2-diaminopropane 4g 2,6-di-tert-butyl-p-cresol. The resulted amount of multi-component synergistic additive was admixed and homogenized with 99kg gasoline having the composition of **table 2**, resulting 100 kg

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of gasoline RON 95, whose octane numbers were measured according to the Standards mentioned in **example 1**; the results are shown in **table 10**.

Tabluel 10.

	Characteristic	Unit	Value	Standard for analysis
5	density 15°C	kg/m ³	739,1	SR EN ISO 3675:03
	RON		98,1	SR EN ISO 5164:06
	MON		86,7	SR EN ISO 5183:06
	final boiling point	C	201,0	SR EN ISO 3405:03
	distillation residue	% v/v	1,3	SR EN ISO 3405:03
10	gums	mg/100mL	2,8	SR EN ISO 6246:00
	manganese	mg/L	6,7	SR EN 14517:05
	Content of oxygen	% m/m	1,6	SR EN 13132:01
	ethanol	% v/v	3,2	SR EN 13132:01
	isopropanol	% v/v	0,1	SR EN 13132:01

References:

- 1 EP0235280
- 2 EP0466511
- 3 EP0476197
- 4 FR1255840
- 5 FR2050841
- 6 GB252019
- 7 GB334181
- 8 GB530597
- 9 RU2005138060
- 10 RU2110561
- 11 RU2117691
- 12 RU2129141
- 13 RU2152981
- 14 RU2184767
- 15 RU2203927
- 16 RU2235117
- 17 US2819953
- 18 US3770397
- 19 US3794473
- 20 US4036605
- 21 US4139349
- 22 US4280458
- 23 US4690687
- 24 US5118325
- 25 US5470358
- 26 WO0116257
- 27 WO2005087901
- 28 WO2006076020
- 29 WO2007105982
- 30 WO2007117176
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CLAIMS

1. A process for obtaining synergistic octane – booster additives containing manganese and gasoline comprising thereof, **characterized in that** the synergistic octane – booster additives are obtained from aromatic amines, preferably N-methyl aniline and organometallic compounds comprising manganese, preferably methylcyclopentadienyl manganese (II) tricarbonyl, dozed so that the weight ratio between Mn and amine or aromatic amines is in the range $>0 - 2,6$ mg Mn/g aromatic amines, preferably $0,5 - 1,0$ mg Mn/g aromatic amines.

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2. The process according to claim 1, **characterized in that** the synergistic octane – booster additives can be formulated also by admixing oxygenated organometallic compounds, such as ethers from alcohols, ethers from phenols or alcohols.

15 3. The process according claim to 1, **characterized in that**, for obtaining gasoline by adding synergistic octane – booster additives, also organometallic compounds belonging to the metal deactivator class, such as N,N-disalicylidene-1,2-diaminopropane and antioxidants belonging to the class of sterically hindered phenols, such as 2,6-di-tert-butyl-p-cresol, can be added, either included in the additive compositions or separately
20 added.

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