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(71) Applicant (for all designated States except US):
CHIMEC S.p.A. [IT/IT]; Via delle Ande 19, I-00144
Roma RM (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **FERRANTE, Gen-
naro** [IT/IT]; Via Michele Guadagno 29, I-80137 Napoli
NA (IT). **BERRA, Alessandra** [IT/IT]; Via Montiglioni
118, I-00046 Grottaferrata RM (IT).

(74) Agents: **GERMINARIO, Claudio** et al.; Società Italiana
Brevetti S.p.A., Piazza di Pietra 39, I-00186 Roma (IT).

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(54) Title: PRODUCTION PROCESS OF UNLEADED HIGH OCTANE NUMBER GASOLINE, AND SO OBTAINED GASO-
LINES

(57) Abstract: In its broadest aspect, the invention relates to eco-sustainable production processes of gasolines or gasoline blends
used as fuel for vehicles with (gasoline- powered) internal combustion engine and controlled ignition including the use of an
emission control additive, which does not damage anti-emission systems of modern vehicles, and so obtained gasolines.



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PRODUCTION PROCESS OF UNLEADED HIGH OCTANE NUMBER
GASOLINE, AND SO OBTAINED GASOLINESDESCRIPTIONTechnical field

5 In its broadest aspect, the invention relates to
eco-sustainable production processes of gasolines or a
gasoline blend used as vehicle fuel including the use of
a non-polluting additive, which does not damage anti-
emission systems of modern vehicles, and so obtained
10 gasolines.

State of the prior art

In the past, old premium grade gasolines were
generally additioned with a lead- (tetraethyl lead) based
organometallic compound, in order to reach an Octane
15 Number (ON) of 84 - 97, with respect to the octane
requirement of the fleet of circulating motor vehicles.

Current gasolines, the so-called green or unleaded
gasolines and the so-called Super Plus gasolines,
respectively reach the Octane Number of 95 and 98/100,
20 which are those required by modern engines, by their
reformulation and/or more and more severe production
processes, with increases in the content of aromatic
compounds (benzene, toluene, xylenes, etc). Moreover, it
is necessary to add compounds of petrochemical origin,
25 the so-called oxygenated compounds, among which the most
widespread is an ether (MTBE).

However, recent technical and legal (environmental)
standards have introduced or are introducing limitations
to the content of both of the abovementioned compound
30 classes.

The use of some aromatic amines, and in particular
of anilines, to increase gasolines' ON has been known
since the early years of the last century.

However, anilines were then described in conjunction
35 with what at the time was the principal additive for ON
boosting, i.e., tetraethyl lead. Subsequently, metallo-
organic compounds (lead, but in some countries also

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manganese) completely superseded the use of anilines, as the former are much more effective.

The situation has completely changed, after the banishment of metallo-organic additives, with the birth
5 of the so-called green (unleaded) gasolines.

Octane Number (ON) is one of the most important parameters of gasoline, as it is directly correlated with power and fuel consumption of the engines in which gasoline is used.

10 In fact, high octane number gasolines allow to design engines with higher performances, generally by increases in the compression ratio. In the past, the octane value of gasolines was improved by resorting to organometallic additives, in the near totality of cases
15 lead-based.

It is known that with the introduction of standards for a strict control of atmospheric pollution, polluting emissions present in motor vehicle exhaust gases have been sensibly reduced in a progressive and continuous
20 way.

Therefore, it has become essential to eliminate from gasolines each and any type of organometallic-based additive.

Alternatively to the use of lead, one of the first
25 approaches utilized was that of increasing the octane level of gasolines by resorting to stricter refining processes.

However, such an approach generally entails an increase in the content of aromatic hydrocarbons in
30 gasolines. These hydrocarbons cause emissions that are highly toxic and noxious to human health; therefore their content in gasolines was progressively reduced, from values often higher than 50% to values even lower than 35%, also through legislative norms.

35 Also the content of the most noxious aromatic hydrocarbon (benzene), it being a very evident carcinogenic, has been reduced from typical values of

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about 3% to <1% values. Further limitations can be envisaged for the future.

In order to increase the Octane Number of gasolines, another widely used approach has been the addition to gasoline of components of non-petroliferous origin: the oxygenated compounds, so-called as characterized by the presence of oxygen in the respective molecules.

These products nearly always exhibit a high Octane Number, therefore they immediately appeared to be valid alternatives to the use of lead-based additives. However, among the several potentially available oxygenated compounds, to date only methyl-ter-butyl-ether (MTBE) has found widespread adoption.

Contraindications generally related to problems of miscibility, reaction to water and interference with other features of the gasolines dissuaded from use of other oxygenated compounds, except in specific countries where, for high availability-related reasons, like e.g. ethyl alcohol in Brazil, other oxygenated compounds (bioethanol) are used.

However, products oxygenated for technical and environmental reasons as a general rule may be utilized only within the limits prescribed by standards for gasoline grades.

Other binding obligations, generally prescribed in the existing standards, which condition gasolines composition are volatility-related ones (vapor pressure and some points of the distillation curve).

The most recent prescriptions derive from the ecological need to limit the so-called evaporation losses, causing introduction of substantial amounts of volatile organic substances (VOCs) into the atmosphere. Obviously, such prescriptions concern, in particular, gasolines distributed in the summer season and in warmer areas.

A further reason allows to forecast for the octane requirement of engines available on the market a tendency

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to increase. This reason derives from the need to abate carbon dioxide emissions ever more.

In this perspective, conceivably engines with higher compression ratios will be designed, so as to significantly reduce fuel consumptions, of course when
5 fed a gasoline having an adequate ON.

However, the need to reformulate gasolines derives not only from standard-prescribed requirements, but also from the evolution of engines. Following the elimination
10 of lead from gasolines, a limited yet generalized reduction of the compression ratios was witnessed, particularly in Europe. This, in order to allow use of gasolines with an ON of 95, in terms of RON (Research Octane Number), lower than that of lead-containing
15 gasolines, which was of 97 or 98 RON. The reason was the need to produce gasoline allowing to minimize the sum of refinery consumptions, related to gasoline production, and those of vehicles.

However, more recently, octane requirement of motor vehicles have begun again to increase. This is
20 essentially due to the introduction of electronic engine management systems, the so-called electronic control units, which allowed to extend knock sensors use to practically all new motor drives. In case a motor vehicle
25 is fed gasoline with an ON lower than the octane requirement of the engine, this device detects any incipient knock phenomena and transmits a signal to the electronic control unit, which instantaneously reduces the spark advance envisaged for those running conditions,
30 and prevents the combustion from going on under a knock regimen.

Availability of these devices allows to optimize engine adjustment conditions with regard to the use of gasolines with a high Octane Number, generally with a RON
35 greater than 95, e.g., 98, 100 or even greater than 100, guaranteeing high performances and low consumptions, yet concomitantly allows the motor vehicle to run acceptably

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even when it is being fed gasolines with an ON lower than the optimal one. Of course, in that case output power will be lower and consumptions higher with respect to the optimal running conditions.

5 As it is well known, the need to reduce all polluting emissions of engines does not concern merely carbon dioxide ones. In fact, for other pollutants such as carbon oxide, unburnt hydrocarbons and nitrogen oxides it dates much earlier. Therefore, engines have
10 progressively been fitted with ever more sophisticated emission control devices and ever more complex feeding systems, which have to be kept free from deposits and uncontaminated by any fuel degradation products, so as to constantly run with the utmost efficiency.

15 From what has been illustrated in the foregoing, it may be inferred that the prior art leaves the following problems unsolved:

- high amounts of aromatic/oxygenated compounds in order to reach the envisaged MON;
- 20 - further refinery difficulties producing high MON gasolines (new High Tech gasolines, with an ON greater than 95, in general of 98-105);
- high stress to plants and apparatuses in order to produce high MON cuts;
- 25 - low chance of directly utilizing "Virgin Naphthas" (straight-run gasolines) and condensates (light hydrocarbons extracted from gas fields).

Scope of the present invention is to provide a solution to the above-indicated problems; in particular,
30 it lies in setting up a process having a low environmental impact for the production of high-quality, low-polluting gasolines.

Summary of the Invention

The present invention is based on the finding that
35 aromatic amines, utilized in the past as mere adjuvants of the action of principal additives for increasing (boosting) the Octane Number, such as the organometallic

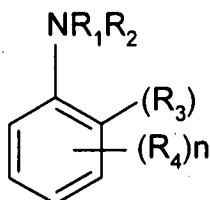
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compounds or the aromatic/oxygenated compounds, can be validly utilized as principal and autonomous ON boosters in state-of the-art unleaded gasolines, characterized by absence of organometallic compounds, low contents of aromatic/oxygenated compounds and low volatility.

Hence, object of a first embodiment of the invention is a production process of a gasoline or a blend of unleaded-type high octane number (ON) gasolines, i.e. with a RON greater than 95, wherein the maximum content of total aromatic compounds is 35% (v/v), the maximum content (v/v) of oxygenated compounds is: methanol 3%, ethanol 5%, isopropanol 10%, t-butanol 10%, ethers having 5 or more Carbon atoms 15%, other oxygenated compounds 10%, and having low volatility, wherein:

the process is operated under low-severity conditions, such as to result in a product having a low octane value (ON), such product is requalified by addition of an aromatic amine-based additive, in an amount comprised between 0.1 % and 3 % (v/v), until obtaining the preset Octane Number. In particular, maximum content of benzene is 1%, and volatility, better expressed as maximum Vapor pressure, is about 100 KPa (or about 1 Bar).

Object of a second embodiment is a process utilizing an aromatic amine having the following formula:



wherein R_1 and R_2 can independently be a hydrogen atom or a methyl, ethyl, n-propyl, iso-propyl, n-butyl, t-butyl, nitrous, phenyl, phenyl-substituted group,

R_3 and R_4 can independently be a hydrogen, fluorine,

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chlorine atom, a methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, ter-butyl, amino, amino(C1-C5)-alkyl-substituted, amino-aryl-substituted group,

n may be 0, 1 or 2,

5 with the proviso that R3 is not hydrogen when n is 0.

Object of a third embodiment is a process wherein the product having a low Octane Number, e.g. ranging from 80 to 95 (RON) or from 75 to 88 MON, is a blend into
10 which low-octane number fractions have been integrated.

In particular, the product is a blend whose components are selected from:

Butane gases mainly containing hydrocarbons having 4 C atoms;

15 Light straight-run gasoline;

C5 isomerate

C6 isomerate

Gasoline reformed with a different degree of severity, in connection with features the end gasoline
20 shall have;

Gasoline from alkylation process;

Light gasoline from cracking process;

Oxygenated components introduced or produced in the same refinery.

25 Object of a further embodiment is a process wherein the low-Octane value product is a straight-run gasoline (sometimes denominated "virgin naphtha" or "light naphtha") or a natural gasoline (sometimes denominated "condensate"), derived from hydrocarbons, liquid at
30 ambient temperature, present in petroleum gas.

Objects of other embodiments are:

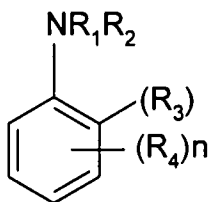
A "green"- or "unleaded"-type gasoline or gasoline blend having a high Octane Number (RON greater than 95), containing an aromatic amine in an amount comprised
35 between 0.1 % and 3 % (v/v), wherein the maximum content of total aromatic compounds is 35% (v/v), the maximum content (v/v) of oxygenated compounds is: methanol 3%,

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ethanol 5%, isopropanol 10%, t-butanol 10%, ethers having 5 or more Carbon atoms 15%, other oxygenated compounds 10%, and having low volatility (i.e., low Vapor pressure - Vapour Pressure - VP) obtainable through the process according to the invention.

A gasoline, or gasoline blend, wherein the maximum content of benzene is 1%, maximum volatility (Vapor pressure) is of about 1 Bar.

A gasoline, or gasoline blend containing from 0.1 to 3% (v/v) of an aromatic amine having the formula:



wherein R_1 and R_2 can independently be a hydrogen atom or a methyl, ethyl, n-propyl, iso-propyl, n-butyl, t-butyl, nitrous, phenyl, phenyl-substituted group,

R_3 and R_4 can independently be a hydrogen, fluorine, chlorine atom, a methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, ter-butyl, amino, amino (C1-C5)-alkyl substituted, amino-aryl-substituted group,

n may be 0, 1 or 2, with the proviso that R_3 is not hydrogen when n is 0.

A gasoline, or gasoline blend, wherein the gasoline supplemented with one or more aromatic amines is a low octane value-type gasoline, like straight-run gasolines (sometimes denominated "virgin naphtha" or "light naphtha") or a natural gasoline (sometimes denominated "condensate"), i.e. derived from hydrocarbons, liquid at ambient temperature, present in petroleum gas, extracted directly at the well mouth.

Finally, object of a further embodiment is the use of a compound containing aromatic amines according to the

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invention for the requalification of hydrocarbon-based extraction products dispersed in oil field gas, called "condensates".

Description of the Invention

5 The solution offered by the present invention is to operate plants and production processes under lower severity conditions (exhausted catalysts, lower temperatures, etc), though producing lower-grade (lower Octane Number) products and requalify the product thus
10 obtained by inclusion of additives that increase its grade, but being not polluting and not falling within the category of the organometallic compounds used in the past to increase the RON and to date totally forbidden.

15 Therefore, the invention offers the possibility of reducing specific energy consumptions maintaining a high grade in the produced gasoline, of preserving plants from excessive stress or wear, by allowing them to produce lower-grade cuts, then raising the grade of the end product by additive use.

20 These processes in particular allow production of high-RON gasoline, reducing aromatic and oxygenated compounds content and end product volatility, complying with the prescriptions defined by the above-reported standards.

25 These processes provide the use of non-polluting and low-concentration (0.1% to 3%) additives, allowing to increase the ON of the novel reformulated gasolines, ON measured both with the "research" method (RON), i.e. ASTM D 2701 or ISO 5164, and with the "motor" method (MON),
30 i.e. ASTM D 2700 or ISO 5163, without increasing the content of aromatic and/or oxygenated compounds, and the vapor pressure (R VP), complying with standard-defined prescriptions, meeting many market requirements in terms of octane grade of the gasolines and offering a valid
35 contribution to the solution of productive problems.

 These processes further allow to increase, in case of need, the RON of a tank of gasoline that does not

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achieve the standards provided, therefore allowing to requalify it to a "nobler" product rather than downgrading it to a fuel with lesser performances.

5 A further application of the present invention is that of making available a blend of end gasoline wherein lower-grade cuts may be introduced, without decreasing end fuel performances therefor.

10 The gasolines or gasoline blends obtained through the process of the invention are products that comply with the provisions of **Standard EN 228**, prescribing gasoline features in the European Community, but used as guidance also in several other Extra-European countries.

15 In particular, these gasolines are characterised by: a maximum aromatic compound content of 35%, a maximum benzene content of 1%, and maximum contents of oxygenated compounds as defined hereinafter:

methanol (max 3%, with mandatory use of cosolvents/stabilizers), ethanol (max 5%), iso-propyl alcohol (max 10%), ter-butyl alcohol (max 10%), ethers
20 with 5 or more carbon atoms (max 15%), other oxygenated compounds (max 10%); moreover, a further limitation is prescribed for the oxygenated compounds in terms of maximum oxygen content allowed, i.e. 2.7%, and a maximum vapor pressure equal to about 1 Bar. This is defined as
25 the partial pressure of gasoline vapors at a set temperature, when equilibrium between liquid phase and gaseous phase is achieved, and measured according to method EN 13016-1).

30 These gasolines comprise an aromatic amine-based compound in an amount comprised between 0.1 % and 3 % (v/v), or between 0.5% and 2%, as additive capable of increasing the ON of low-octane gasolines.

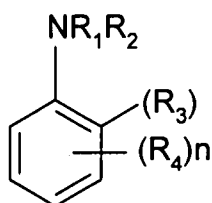
35 The gasolines according to the invention are gasolines reformulated soon after elimination of organometallic additives, both lead-based and other metal-based ones (so-called unleaded gasoline).

Addition of the aromatic amines of the invention to

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reformulated gasolines yields a high-ON fuel with a RON value greater than 95, e.g. 96, 97, 98, 99, 100, 101, 102, 103, 104 or 105, the so-called Super Plus gasoline, and gasolines having a high degree of stability and of
 5 deterging power, i.e., capable of opposing a fouling tendency in the feeding system.

The additive of the invention consists in an aromatic amine having the formula:



10

wherein R_1 and R_2 can independently be a hydrogen atom or a methyl, ethyl, n-propyl, iso-propyl, n-butyl, t-butyl, nitrous, phenyl, phenyl-substituted group,

15 R_3 and R_4 can independently be a hydrogen, fluorine, chlorine atom, a methyl, ethyl, n-propyl, iso-propyl, n-butyl, isobutyl, ter-butyl, amino, amino(C1-C5)-alkyl-substituted, amino-aryl-substituted group,

n may be 0, 1 or 2, with the proviso that R_3 is not
 20 hydrogen when n is 0,

Examples of aromatic amines useful in the present invention are:

2-fluoroaniline, 2-chloroaniline, N-methylaniline; ortho-toluidine; ortho-ethylaniline; N-methyl-ortho-toluidine; 2,4-dimethylaniline; 2,3-dimethylaniline; 2,5-dimethylaniline; 2,6-dimethylaniline; N-methyl-2,4-dimethylaniline; N-nitrosodiphenylamine; N-methyl-2,3-dimethylaniline; N-methyl-2,6-dimethylaniline, N-ethyl-aniline, N-phenyl-aniline, N-propyl-aniline, N-isopropyl-aniline, N-isobutyl-aniline, N-ter-butyl-aniline, N-isoamyl-aniline, 2-methyl-3-fluoroaniline, 2-fluoro-3-methylaniline, 2-methyl-4-fluoroaniline, 2-fluoro-4-methylaniline, 2,5-dimethyl-3-fluoroaniline, 2,5-dimethyl-4-fluoroaniline, 2,3-dimethyl-6-fluoroaniline,

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2-fluoro-3-ethylaniline, 2-ethyl-4-fluoroaniline, 2-methyl-5-ethyl-4-fluoroaniline, 2-fluoro-6-isopropylaniline, 2-isopropyl-3-fluoro-5-ethyl-aniline, 2,6-di-ter-butyl-4-fluoroaniline, N-Nitrosodiphenylamine, N,N-Dimethyl-p-phenylendiamine, N,N-Diethyl-p-phenylendiamine
5 and any possible mixture thereof.

The aromatic amine compositions can contain other additives suitable for improving specific properties, like e.g. antioxidants, metal deactivators, corrosion
10 inhibitors, deposit modifiers and detergents.

The abovementioned amine compounds allow to obtain an improvement of the ON in any type of gasoline, both in terms of RON, i.e. the ON measured with the "research" method (ASTM D 2699 or ISO 5164) and in terms of MON,
15 i.e. the ON measured with the "motor" method (ASTM D 2700 or ISO 5163).

Without binding the scope of the present invention to specific theories, the mechanism underlying the anti-knock function of the molecules subject-matter of the
20 present invention is deemed to be as follows: high-energy free radicals attack the substances subject-matter of the invention, with formation of neutral molecules and new free radicals, whose relative stability allows to control the extent of chain reaction propagation and, therefore,
25 allows the molecules at issue to exert their antiknock effect.

Several are the advantages offered by the present invention:

- possibility of recovery of a non-specification
30 tank, avoiding costly and lengthy reformulation and remixing operations;
- possibility of using lower-grade cuts;
- possibility of operating with lower-severity plant conditions, lowering internal consumptions of the
35 refineries and reducing greenhouse effect gas emissions thereof;
- possibility of using condensates without

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processing them;

- avoiding situations of unfeasibility of production of high-Octane Number gasoline, enabling vehicles fitted with a knock sensor to operate under attitude conditions of optimal adjustment (maximum power/minimum consumptions);

- possibility of maximizing the production of high-octane gasoline, so as to facilitate design of engines having a high compression ratio, hence high efficiency, in order to allow reduction of fuel consumptions and therefore of greenhouse effect gas (carbon dioxide) emissions in the transportation field;

- possibility of completely removing oxygenated products from gasolines, improving engine efficiency by the introduction of a greater energy content per cycle, that is, preventing introduction of oxygen with the fuel.

In its various embodiments, the present invention can be applied to the following gasoline compositions:

State-of-the-art unleaded gasolines (Super plus gasoline), intended to be used in electronic system-managed motor drives (e.g., Euro III, Euro IV and Euro V), characterized as follows.

RON: 90 - 105

MON: 80 - 95

Sulphur content: 0 - 10 mg/kg

Oxidation stability (EN ISO 7536): 360 - 580 min

Existent gum content (EN ISO 6246): 1- 5 mg/kg

Aromatic hydrocarbon content: 5 - 35 % (v/v)

Olefinic hydrocarbon content: 0 - 18 % (v/v)

Benzene content: 0.1 - 1 % (v/v)

Oxygen content: 0.01 - 3.5 % (v/v)

Methanol content: 0 - 3 % (v/v)

Ethanol content: 0 - 10 % (v/v)

Iso-propyl alcohol content: 0 - 10 % (v/v)

Isobutyl alcohol content: 0 - 10 % (v/v)

Ter-butyl alcohol content: 0 - 7 % (v/v)

≥5 C atom ether content: 0 - 15 % (v/v)

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Other oxygenated compound content: 0 - 10 % (v/v)

Generally, these gasolines are produced by suitably mixing components obtained in refineries, with respect to their plant configuration. Principal components used are the following:

Butane gases (mainly containing hydrocarbons having 4 C atoms);

Light straight-run gasoline;

C5 isomerate

10 C6 isomerate

Reformed gasoline (with a different degree of severity in connection with features the end gasoline shall have);

Gasoline from alkylation process;

15 Light gasoline from cracking process;

Oxygenated compounds introduced or produced in the same refinery, generally MTBE.

Moreover, apart from ON boosters, they can contain additives suitable for improving specific properties, like, e.g., antioxidants, metal deactivators, corrosion inhibitors, deposit modifiers and detergents.

Production of these gasolines can be very difficult (sometimes unfeasible) and costly, with regard to the need to balance high octane grade with all other technical and environmental requirements. In the first place, among those, aromatics and benzene content, as well as restrictions on use of oxygenated products and volatility features.

In these gasolines, aromatics content can conveniently be controlled by reducing the severity of the reforming process (which transforms linear-chain paraffinic hydrocarbons into cyclic, mainly aromatic hydrocarbons through a dehydrogenation mechanism). Olefinic hydrocarbon content can instead be controlled by reducing the amounts of gasoline from cracking used.

However, octane contribution provided by these components is concomitantly lowered, therefore possible

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octane deficiencies can conveniently be compensated for by resorting to the additives subject-matter of the present invention. The same can be done in case the balance between octane grade and oxygenated product content requires to limit the use of these products. In fact, oft-times the production of high-octane level gasoline (>95 RON) proves unfeasible, even when maximizing, within Standard-prescribed limits, the content of aromatics and oxygenated compounds.

10 In another embodiment, the gasoline according to the invention is a gasoline having a low octane value, such as straight-run gasolines (sometimes denominated "virgin naphtha" or "light naphtha") or a natural gasoline (sometimes denominated "condensate"), i.e., derived from hydrocarbons, liquid at ambient temperature, present in petroleum gas, extracted directly at the mouth of the oil well. These products mainly contain saturated linear-chain hydrocarbons, and therefore are characterized by relatively low octane values.

20 They generally exhibit a RON between 65 and 70, therefore applying the present invention allows to increase this ON also up to values of 85 - 90, so as to allow their use on motor drives for which a high combustion efficiency is not required, or to allow their use as semi-processed products, to be used for the formulation of higher-grade gasolines.

The present invention also relates to the use of a compound including aromatic amines in the management of virgin naphtha refineries: in fact, a naphtha cut usually exhibits a low RON and therefore is normally intended to be reprocessed in other plants, such as Catalytic Reforming and Isomerization ones.

35 Both of the indicated processings entail as an end effect that of increasing naphtha RON, but with heavy contraindications. In fact, some naphthas cannot be processed, in particular in Isomerization, as having an overly wide boiling range. This entails a big effort at

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selecting naphtha cuts by the refinery, and a consequent impact on high-RON cut production capabilities, and difficulties in its introduction in the blending of the end gasoline. In fact, naphthas with an unsuitable range must be sent to other purposes.

With the use of the compound including the aromatic amine the whole problem is bypassed, it being possible to directly act by increasing the RON on any naphtha, with no restriction whatsoever.

Moreover, Isomerization plant use causes an increase in vapor pressure of the naphtha that, overstepping commercial specification values, cannot be introduced into gasoline unless below certain percentages. The compound including aromatic amines allows use of all of the naphtha and does not increase the vapor pressure of the gasoline blend, tending instead to decrease it.

The present invention also relates to the use of a compound including aromatic amines for an oil field extraction product, i.e. the "condensates" that define gas-dispersed hydrocarbons and therefore are entrained by the flow of an extraction well, and subsequently isolated into suitable separators; they may be light hydrocarbons or even rather heavy ones, usually paraffinic hydrocarbons.

In some producing countries, essentially North Africa, Russia, etc, "condensates" from gas extraction fields have features very similar to those of gasolines, constituting a possible component of the blend of end gasolines. In general, however, those are components which lower the RON of the end product, or that anyhow do not give a RON meeting market-required values. Therefore, availability of an additive that could make a gas field condensate directly useful, with no significant intermediate processing (isomerization or cracking) might have a very high added value. This is so since the condensate could be additioned and used on its extraction area, with no need of transportation, significant

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processing and blending.

Another advantage of the aromatic amine-based compound is that of allowing introduction into the end gasoline of cuts from Fluid Catalytic Cracking and Thermal Cracking (refining and petrochemical), which usually have a high RON (not accepted by car makers) but a much worse MON. The compound subject-matter of the patent allows to raise the MON of these cuts, which therefore can be used directly, without undergoing further processing; this entails once again a remarkable reduction of specific energy consumptions.

Moreover, it is found that within the extent of the end stage of the production process of any type of the aforementioned gasolines, i.e. the blending of the different components in order to obtain the end product, it frequently happens that such a material does not comply with octane grade limitations, for a few tenths of point of RON, MON or of both.

Therefore, a further amount of one of the high-ON components has to be added. However, this operation is not always possible due to lack of available volume in the blending tank, as well as of a possible additional tank. Moreover, adding additional quantities of one of the components entails the risk of modifying other features of the end gasoline composition, e.g. the aromatics content, or chemico-physical features, e.g. distillation, vapor pressure, etc.

On the contrary, any correction to the Octane Number by resorting to the present invention allows not to incur such problems. In fact, the addition of a small amount of additive does not require availability of further mixability, nor does it modify other end gasoline features. At the same time, it significantly reduces the technical times for effecting the correction and allows work and energy saving.

Further advantages, features and operation steps of the present invention will be made apparent in the

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following detailed description of some examples thereof relates to a series of applications given by way of example and not for limitative purposes.

Testing

Example 1

A series of aromatic amines subject-matter of the present invention were evaluated in state-of-the-art unleaded gasolines (intended to be used in motor drives managed by Euro III, Euro IV and Euro V electronic system), always using the same test pattern.

Hereinafter, average results are reported related to octane performances obtained with reference aromatic amine 2,4-dimethylaniline, and with various other amines according to the invention.

2,4-dimethylaniline: 1.0
N-Nitrosodiphenylamine: 2.5
N,N-Dimethyl-p-phenylendiamine: 1.8
N,N-Diethyl-p-phenylendiamine: 1.8
N-methylaniline: 0.8
2,6-dimethylaniline: 0.7
3,5-dimethylaniline: 0.7
2,3-dimethylaniline: 0.6
2,5-dimethylaniline: 0.5

Example 2

Testing was conducted on various gasolines having typical features of products to which the present invention applies. Therefore, each of these formulations was supplemented with different dosages of 2,4-dimethylaniline containing an aromatic amine, and each of the samples thus obtained was analyzed in a laboratory by performing RON and MON measuring, with methods ISO 5164 (ASTM D 2699) and ISO 5163 (ASTM D 2700).

All results were statistically processed, performing a linear regression of the data (applying the method of least squares), in order to check octane response pattern in each formulation.

Aromatic amines used in the present example are

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selected from:

N-methylaniline; 2,4-dimethylaniline; 2,3-dimethylaniline; 2,5-dimethylaniline; 2,6-dimethylaniline; N-ethyl-aniline, N-phenyl-aniline, N-propyl-aniline, N-isopropyl-aniline, N-isobutyl-aniline, N-ter-butyl-aniline, N-isoamyl-aniline, N-Nitrosodiphenylamine, N,N-Dimethyl-p-phenylendiamine, N,N-Diethyl-p-phenylendiamine or mixture thereof.

As low-ON gasolines, state-of-the-art unleaded gasolines were used, having an ON respectively of between 90 and 98 (RON) and 80 and 88 (MON), characterized as follows:

lead content: 0 mg/kg
Other metal content: 0 mg/kg
Sulphur content: 0 - 10 mg/kg
Oxidation stability (EN ISO 7536): 360 - 580 min
Existent gum content (EN ISO 6246): 1- 5 mg/kg
Aromatic hydrocarbon content: 5 - 35 % (v/v)
Olefinic hydrocarbon content: 0 - 18 % (v/v)
Benzene content: 0.1 - 1 % (v/v)
Oxygen content: 0.01 - 3.5 % (v/v)
Methanol content: 0 - 3 % (v/v)
Ethanol content: 0 - 10 % (v/v)
Iso-propyl alcohol content: 0 - 10 % (v/v)
Isobutyl alcohol content: 0 - 10 % (v/v)
Ter-butyl alcohol content 0 - 7 % (v/v)
5+ C atom ether content: 0 - 15 % (v/v)

Other oxygenated compound content: 0 - 10 % (v/v), wherein these gasolines generally are produced by suitably blending the components obtained in refineries, in connection with their plant configuration.

Main components used in this gasoline are the following ones:

Butane gases (mainly containing hydrocarbons having 4 C atoms);
Light straight-run gasoline;
C5 isomerate

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C6 isomerate

Reformed gasoline (with a different degree of severity in connection with features the end gasoline shall have);

- 5 Gasoline from alkylation process;
Light gasoline from cracking process;
Oxygenated compounds introduced or produced in the same refinery, generally MTBE.

10 The results, in terms of dosage in % (v/v) by 1-point increase of RON or MON, were respectively: 0.3%(v/v)/RON and 0.5%(v/v)/MON.

Response curve pattern: linear ($R^2 > 0.9$).

Example 3.

15 The example relates to gasolines having a low octane value, such as straight-run gasolines (sometimes denominated "virgin naphtha" or "light naphtha") or natural gasolines (sometimes denominated "condensates"), i.e., hydrocarbons, liquid at ambient temperature, present in petroleum gas, extracted directly at the mouth
20 of the oil well. The products mainly contain saturated linear-chain hydrocarbons and therefore are characterized by relatively low octane values, having base product RON and MON ranging respectively between 85 and 90 (RON) and 75 and 80 (MON).

25 These gasolines were supplemented with different dosages of 2,4-dimethylaniline.

Results, in terms of dosage in % (v/v) by 1-point increase of RON or MON, were: 0.25%(v/v)/RON and 0.40%(v/v)/MON. Response curve pattern: linear ($R^2 >$
30 0.9).

To confirm the above-mentioned results, a first check test with 2,4-dimethylaniline was performed. RON response was evaluated by utilizing the following simulated base blend of gasoline:

35 Isomerate: 41.5%
Platformate: 55.5%
Condensate: 3.0%

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The results are reported hereinafter in Table 1

Table 1

Test No.	Isomerase	Platformate	Condensate	2,4-dimethylaniline	2,4-dimethylaniline	RON	VP
				ml in 500ml	Dosage v/v%		Bar
Measure 1	0.415	0.555	0.030	0.000	0.000	94.30	0.530
Measure 2	0.415	0.555	0.030	4.00	0.80	97.10	0.517

Subsequently, a second check test with 2,4-dimethylaniline was performed:

5 RON response was evaluated by utilizing the following simulated base blend of gasoline:

Isomerase: 47.0%

Platformate: 50.0%

Condensate: 3.0 %

10 The result is reported hereinafter in Table 2

Table 2

Test No.	Isomerase	Platformate	Condensate	2,4-dimethylaniline	2,4-dimethylaniline	RON	VP
				ml in 500ml	Dosage % v/v		Bar
Measure 1	0.47	0.50	0.03	0.000	0.000	93.50	0.573
Measure 2	0.47	0.50	0.03	1.000	0.200	94.40	0.563
Measure 3	0.47	0.50	0.03	4.50	0.90	96.00	0.550

In particular, it was found that the use of the aromatic amine can aid the refining in increasing the isomerase number in the gasoline blend.

15 A dose of aromatic amine of about 3000 ppm by volume

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causes a RON increase in the treated blend of 1 RON unit, and a minimum of 0.5 MON units.

Moreover, it was observed that for each addition of 3000 ppm (by volume) of amine, treated gasoline vapor pressure (VP) is reduced by 1%, as can be seen from the
5 second check test.

Examples 4 to 9

As to state-of-the-art unleaded gasolines, intended to be used in motor drives managed by an electronic
10 system, e.g., Euro III, Euro IV and Euro V, several other examples of application of 2,4-dimethylaniline were developed. Such examples relate to formulations of real gasolines, i.e., product lots refinery-prepared in industrial amounts for introduction on the market, which
15 utilized the present invention for achievement of compliance with octane grade limits provided for by standards in force.

For each of these examples, as well as for the other examples indicated in the foregoing, results are reported
20 in terms of dosage corresponding to 1-point increases of RON and MON, as well as linear regression coefficients (R2) of the regression line related to results obtained at the various dosages subjected to tests.

Example 4

25 Dosages, for 1-point increase respectively of RON and MON, were: 0.25 % (v/v) and 0.33 % (v/v), with R2=1.00 for RON and =0.98 for MON.

Example 5.

30 Dosages, for 1-point increase respectively of RON and MON, were: 0.19 % (v/v) and 0.34 % (v/v), con R2=0.96 for RON and =0.99 for MON.

Example 6.

35 Dosages, for 1-point increase respectively of RON and MON, were: 0.34 % (v/v) and 0.44 % (v/v), with R2=0.98 for RON and =0.99 for MON.

Example 7.

Dosages, for 1-point increase respectively of RON

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and MON, were: 0.22 % (v/v) and 0.32 % (v/v) with $R_2=1.00$ for RON and $=0.99$ for MON.

Example 8.

Dosages, for 1-point increase respectively of RON
5 and MON, were: 0.22 % (v/v) and 0.34 % (v/v) with $R_2=0.99$ for RON and $=0.97$ for MON.

Example 9.

Dosages, for 1-point increase respectively of RON
and MON, were: 0.24 % (v/v) and 0.40 % (v/v) with $R_2=0.99$
10 for RON and $=0.95$ for MON.

Examples 10, 11 and 12

Some amines, evaluated in state-of-the-art unleaded
gasolines, intended to be used in motor drives managed by
an electronic system, e.g. Euro III, Euro IV and Euro V,
15 exhibit dosages for 1-point increases respectively of RON
and MON, in some cases lower than 2,4-dimethylaniline
(see examples 4 to 9), denoting higher efficiency.

Example 10

N-Nitrosodiphenylamine:

20 dosage for 1-point increase of RON = 0.11 % (v/v);
dosage for 1-point increase of MON = 0.28 % (v/v);

N,N-Dimethyl-p-phenylendiamine:

dosage for 1-point increase of RON = 0.15 % (v/v);
dosage for 1-point increase of MON = 0.23 % (v/v);

25 N,N-Diethyl-p-phenylendiamine:

dosage for 1-point increase of RON = 0.15 % (v/v);
dosage for 1-point increase of MON = 0.25 % (v/v);

Example 11

N-Nitrosodiphenylamine:

30 dosage for 1-point increase of RON = 0.15 % (v/v);
dosage for 1-point increase of MON = 0.21 % (v/v);

N,N-Dimethyl-p-phenylendiamine:

dosage for 1-point increase of RON = 0.18% (v/v);
dosage for 1-point increase of MON = 0.29 % (v/v);

35 N,N-Diethyl-p-phenylendiamine:

dosage for 1-point increase of RON = 0.19 % (v/v);
dosage for 1-point increase of MON = 0.33 % (v/v);

Example 12

N-Nitrosodiphenylamine:

dosage for 1-point increase of RON = 0.11 % (v/v);

dosage for 1-point increase of MON = 0.16 % (v/v);

5 N,N-Dimethyl-p-phenylendiamine:

dosage for 1-point increase of RON = 0.15 % (v/v);

dosage for 1-point increase of MON = 0.18 % (v/v);

N,N-Diethyl-p-phenylendiamine:

dosage for 1-point increase of RON = 0.15 % (v/v);

10 dosage for 1-point increase of MON = 0.19 % (v/v);

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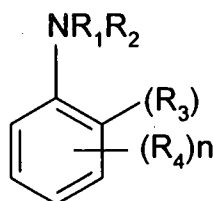
CLAIMS

1. A production process of a premium grade "unleaded"-type gasoline or gasoline blend having an Octane Number (ON) (RON) greater than 95, wherein the maximum content of total aromatic compounds is 35% (v/v),
5 the maximum content (v/v) of oxygenated compounds is: methanol 3%, ethanol 5%, isopropanol 10%, t-butanol 10%, ethers having 5 or more Carbon atoms 15%, other oxygenated compounds 10%, and having low vapor pressure,
10 wherein:

the process is operated under low-severity conditions, such as to result in a product having a low octane value (ON), such product is requalified by addition of an aromatic amine-based additive, in an
15 amount comprised between 0.1 % and 3 % (v/v), until obtaining the preset Octane Number.

2. The process according to claim 1, wherein maximum content of benzene is 1% and maximum vapor pressure is equal to about 1 Bar.

20 3. The process according to claim 2, wherein the aromatic amine has the following formula:



25

wherein R_1 and R_2 can independently be a hydrogen atom or a methyl, ethyl, n-propyl, iso-propyl, n-butyl, t-butyl, nitrous, phenyl, phenyl-substituted group,

30 R_3 and R_4 can independently be a hydrogen, fluorine, chlorine atom, a methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, ter-butyl, amino, amino(C1-C5)-alkyl-substituted, amino-aryl-substituted group, and

n may be 0, 1 or 2,

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with the proviso that R3 is not hydrogen when n is 0.

4. The process according to claim 3, wherein the aromatic amine is selected from the group:

5 2-fluoroaniline, 2-chloroaniline, N-methylaniline;
ortho-toluidine; ortho-ethylaniline; N-methyl-
orthotoluidine; 2,4-dimethylaniline; 2,3-dimethylaniline;
2,5-dimethylaniline; 2,6-dimethylaniline; N-methyl-2,4-
dimethylaniline; Ni-nitrosodiphenylamine; N-methyl-2,3-
10 dimethylaniline; N-methyl-2,6-dimethylaniline, N-ethyl-
aniline, N-phenyl-aniline, N-propyl-aniline, N-isopropyl-
aniline, N-isobutyl-aniline, N-ter-butyl-aniline, N-
isoamyl-aniline, 2-methyl-3-fluoroaniline, 2-fluoro-3-
methylaniline, 2-methyl-4-fluoroaniline, 2-fluoro-4-
15 methylaniline, 2,5-dimethyl-3-fluoroaniline, 2,5-
dimethyl-4-fluoroaniline, 2,3-dimethyl-6-fluoroaniline,
2-fluoro-3-ethylaniline, 2-ethyl-4-fluoroaniline, 2-
methyl-5-ethyl-4-fluoroaniline, 2-fluoro-6-isopropyl-
aniline, 2-isopropyl-3-fluoro-5-ethyl-aniline, 2,6-di-
20 ter-butyl-4-fluoroaniline, N-Nitrosodiphenylamine, N,N-
Dimethyl-p-phenylendiamine, N,N-Diethyl-p-phenylendiamine
and any possible mixture thereof.

5. The process according to any one of the claims 1 to 4, wherein the product having a low octane number is
25 a blend into which low-octane number fractions have been
integrated.

6. The process according to any one of the claims 1 to 5, wherein the product is a blend whose components are selected from:

30 Butane gases mainly containing hydrocarbons having 4
C atoms;

Light straight-run gasoline;

C5 isomerate

C6 isomerate

35 Gasoline reformed with a different degree of
severity, in connection with features the end gasoline
shall have;

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Gasoline from alkylation process;

Light gasoline from cracking process;

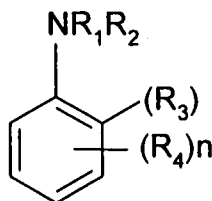
Oxygenated components introduced or produced in the same refinery.

5 7. The process according to any one of the claims 1 to 5, wherein the low-Octane value product is a straight-run gasoline (sometimes denominated "virgin naphtha" o "light naphtha") or a natural gasoline (sometimes denominated "condensate"), derived from
10 hydrocarbons, liquid at ambient temperature, present in petroleum gas.

8. An "unleaded-type" gasoline, or gasoline blend, having an Octane Number (RON) greater than 95, containing an aromatic amine in an amount comprised between 0.1 %
15 and 3 % (v/v), wherein the maximum content of total aromatic compounds is 35% (v/v), the maximum content (v/v) of oxygenated compounds is: methanol 3%, ethanol 5%, isopropanol 10%, t-butanol 10%, ethers having 5 or more Carbon atoms 15%, other oxygenated compounds 10%,
20 and having low vapor pressure, obtainable through the process according to any one of the claims 1 to 7.

9. The gasoline, or gasoline blend, according to claim 8, wherein the maximum content of benzene is 1%, the maximum vapor pressure is equal to about 1 Bar.

25 10. The gasoline, or gasoline blend, according to any one of the claims 8 or 9, containing from 0.1 to 3% (v/v) of an aromatic amine having the formula:



30

wherein R_1 and R_2 can independently be a hydrogen atom or a methyl, ethyl, n-propyl, iso-propyl, n-butyl,

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t-butyl, nitrous, phenyl, phenyl-substituted,

R3 and R4 can independently be a hydrogen, fluorine, chlorine atom, a methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, ter-butyl, amino, amino(C1-C5)-alkyl-substituted, amino-aryl-substituted group,

n may be 0, 1 or 2, with the proviso that R3 is not hydrogen when n is 0.

11. The gasoline, or gasoline blend, according to any one of the claims 8 or 10, wherein the aromatic amine is selected from the group:

2-fluoroaniline, 2-chloroaniline, N-methylaniline; ortho-toluidine; ortho-ethylaniline; N-methyl-orthotoluidine; 2,4-dimethylaniline; 2,3-dimethylaniline; 2,5-dimethylaniline; 2,6-dimethylaniline; N-methyl-2,4-dimethylaniline; N-nitrosodiphenylamine; N-methyl-2,3-dimethylaniline; N-methyl-2,6-dimethylaniline, N-ethylaniline, N-phenyl-aniline, N-propyl-aniline, N-isopropylaniline, N-isobutyl-aniline, N-ter-butyl-aniline, N-isoamyl-aniline, 2-methyl-3-fluoroaniline, 2-fluoro-3-methylaniline, 2-methyl-4-fluoroaniline, 2-fluoro-4-methylaniline, 2,5-dimethyl-3-fluoroaniline, 2,5-dimethyl-4-fluoroaniline, 2,3-dimethyl-6-fluoroaniline, 2-fluoro-3-ethylaniline, 2-ethyl-4-fluoroaniline, 2-methyl-5-ethyl-4-fluoroaniline, 2-fluoro-6-isopropylaniline, 2-isopropyl-3-fluoro-5-ethyl-aniline, 2,6-di-ter-butyl-4-fluoroaniline, N-Nitrosodiphenylamine, N,N-Dimethyl-p-phenylendiamine, N,N-Diethyl-p-phenylendiamine and any possible mixture thereof.

12. The gasoline, or gasoline blend, according to claim 8, wherein the gasoline supplemented with one or more aromatic amines is a gasoline obtained without lead (unleaded) of the type intended to be used in motor drives managed by an electronic system, Euro III, Euro IV and Euro V, having the following formula:

RON: 90 - 105

MON: 80 - 95

Sulphur content: 0 - 10 mg/kg

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Oxidation stability (EN ISO 7536): 360 - 580 min

Existent gum content (EN ISO 6246): 1- 5 mg/kg

Aromatic hydrocarbon content: 5 - 35 % (v/v)

Olefinic hydrocarbon content: 0 - 18 % (v/v)

5 Benzene content: 0.1 - 1 % (v/v)

Oxygen content: 0.01 - 3.5 % (v/v)

Methanol content: 0 - 3 % (v/v)

Ethanol content: 0 - 10 % (v/v)

Iso-propyl alcohol content: 0 - 10 % (v/v)

10 Isobutyl alcohol content: 0 - 10 % (v/v)

Ter-butyl alcohol content 0 - 7 % (v/v)

5+ C atom ether content: 0 - 15 % (v/v);

Other oxygenated compound content: 0 - 10 % (v/v);

13. The gasoline, o gasoline blend, according to
15 claim 8, wherein the gasoline supplemented with one or
more aromatic amines is a low octane value-type gasoline,
like straight-run gasolines (sometimes denominated
"virgin naphtha" o "light naphtha") or a natural gasoline
(sometimes denominated "condensate"), i.e., derived from
20 hydrocarbons, liquid at ambient temperature, present in
petroleum gas, extracted directly at the mouth of the oil
well.

14. Use of a compound containing aromatic amines
according to claims 10 or 11 for the requalification of
25 hydrocarbon-based extraction products dispersed in oil
field gas, called "condensates".