(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 310 545 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:
14.05.2003 Bulletin 2003/20

(21) Application number: **01934381.3**

(22) Date of filing: **28.05.2001**

(51) Int Cl.^{7}: **C10L 1/12**, C10L 1/30

(86) International application number:
PCT/JP01/04474

(87) International publication number:
WO 01/096502 (20.12.2001 Gazette 2001/51)

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR

(30) Priority: **14.06.2000 JP 2000178525**

(71) Applicant: **I.B.E. Co., Ltd.**
Aichi 444-0703 (JP)

(72) Inventor: **MAKINO, Shinji, c/o I.B.E. Co Ltd.**
Hazu-gun, Aichi 444-0703 (JP)

(74) Representative: **VOSSIUS & PARTNER**
Siebertstrasse 4
81675 München (DE)

(54) FUEL MODIFIER

(57) The object of the present invention is to improve the efficiency of combustion of fuel and to reduce toxic components contained in the combustion gas. To attain the object in the present invention, an iron salt is added in fuel such as gasoline, kerosene, light oil, heavy oil and the like as a fuel modifier

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] The present invention relates to a fuel modifier.

PROBLEMS TO BE SOLVED

[0002] Problems to be solved are improving combustion efficiency and reducing production of carbon monoxide CO and NOX.

DISCLOSURE OF THE INVENTION

[0003] The present invention provides a fuel modifier comprising an iron salt as a means to solve said problems. Generally, said fuel modifier is provided by adding and mixing an alcohol solution of said iron salt to a mineral oil. Said iron salt is ferric-ferrous iron salt and/or ferrous iron salt and/or ferric iron salt.

PRECISE DESCRIPTION OF THE INVENTION

[0004] The fuel modifier of the present invention comprises ferric-ferrous iron salt and/or ferrous iron salt and/or ferric iron salt.

[FERROUS IRON SALTS, FERRIC IRON SALTS]

[0005] Ferrous iron salts and/or ferric iron salts used as the fuel modifier in this invention include inorganic acid salts such as hydrochloride, sulfate, nitrate, phosphate and the like, organic acid salts such as acetate, formate, oxalate, citrate and the like, mixtures thereof. Two or more kinds of ferrous iron salts and/or ferric iron salts may be used together.

[FERRIC-FERROUS IRON SALTS]

[0006] Ferric-ferrous iron salt of the present invention is iron salt having properties between ferrous iron salt and ferric iron salt and said iron salt is such as inorganic acid salts (e.g. hydrochloride, sulfate, phosphate, nitrate and the like), organic acid salts (e.g. formate, acetate, propionate and the like). Said ferric-ferrous iron salt is prepared by putting ferric iron salt in a large quantity of strong alkaline aqueous solution such as sodium hydroxide, potassium hydroxide, lithium hydroxide, calcium hydroxide and the like to cause valence conversion from ferric iron to ferrous iron or putting ferrous iron salt in a large quantity of strong acid aqueous solution such as hydrochloride acid, sulfuric acid and the like to cause valance conversion from ferrous iron to ferric iron and said ferric-ferrous iron salt is obtained as transition form during said valence conversion. Concrete illustrations of methods of production of said ferric-ferrous iron salt are shown hereafter.

[0007] Commonly, two methods described below are applied to prepare said ferric-ferrous iron salt.

1. Method 1 (Preparation from ferric iron salt)

[0008] Ferric chloride ($FeCl_3 \cdot 6H_2O$), 1.0 mg was dissolved in 100 ml of 0.5 N sodium hydroxide aqueous solution and stirred, then the solution was allowed to stand for overnight. After filtering out some insoluble products in the solution, the solution was neutralized with hydrochloric acid then concentrated in a reduced pressure desiccator to get a dried and crystallized product. Thus the crystallized product with sodium chloride, that is, chloride of ferric-ferrous iron (hereinafter sometimes referred to as iron chloride (II, III)), was prepared.

In case of extracting iron chloride (II, III) from the crystallized product with sodium chloride, the product was dissolved in 50 ml of 80% by weight isopropyl alcohol aqueous solution to elute iron chloride (II, III). After separating the solution containing eluted iron chloride (II, III), the solution was concentrated at reduced pressure in order to remove the solvent and dry. Then the procedure consisting of elution, concentration and dry was repeated a few times. Thus iron chloride (II, III), 0.25 mg was extracted from the crystallized product with sodium chloride.

2. Method 2 (Preparation from ferrous iron salt)

[0009] Ferrous sulfate ($FeSO_4 \cdot 7H_2O$), 1.0 mg was dissolved in 100 ml of 0.5 N HCl aqueous solution and stirred, then the solution was allowed to stand for overnight. After filtering out some insoluble products in the solution, the solution was concentrated in a reduced pressure desiccator to get a dried product. The dried product in powder was dissolved in 10 ml of 80% by weight isopropyl alcohol aqueous solution to elute iron chloride (II, III). After separating the solution containing eluted iron chloride (II, III), the solution was concentrated at reduced pressure in order to remove the solvent and dry. Then the procedure consisting of elution, concentration and dry was repeated a few times. Thus iron chloride (II, III), 0.6 mg was extracted from the crystallized product with sodium chloride.

Ferric-ferrous iron salts in this invention may include other compounds such as inorganic compounds (e.g. sodium chloride, sodium sulfate, ammonium chloride, ammonium sulfate, zinc chloride, zinc sulfate, zinc oxide, zinc hydroxide, zinc acetate, diatomite, bentonite, silica, alumina and the like), organic compounds (e.g. vitamin, hormone, protein, lipid and the like). In the case of using the ferric-ferrous iron salt including other compound, its ability is not changed.

[PREPARATION OF THE FUEL MODIFIER]

[0010] To prepare said fuel modifier of the present invention, said ferric-ferrous iron salt and/or ferrous iron salt and/or ferric iron salt is(are) dissolved in an alcohol such as ethyl alcohol, isopropyl alcohol, normal butyl alcohol, isobutyl alcohol, tertiary butyl alcohol, and the like, or solvent mixture of said alcohol(s) and water and then said solution is added to mix to a petroleum solvent such as gasoline, kerosene, light oil and the like. Generally, the resulting fuel modifier of the present invention contains 1 to 5 ppm of ferric-ferrous iron salt and/or ferrous iron salt and/or ferric iron salt.

[FUEL MODIFICATION]

[0011] Generally, about 0.1 to 1.0 ml of said fuel modifier of the present invention is added to 1000 ml of the fuel such as gasoline, kerosene, light oil, heavy oil and the like. In said fuel modifier modified by said fuel modifier, the combustion efficiency is improved and production of toxic substance such as CO, NOX and the like are suppressed.

[EFFECT OF THE INVENTION]

[0012] In said fuel modified by said fuel modifier, the combustion efficiency is improved and when said fuel is used as fuel of the car, the efficiency of fuel consumption is much improved and content of toxic substance such as CO, NOX and the like in exhaust gas is much reduced.

[Example 1]

[0013] Ferrous sulfate ($FeSO_4 \cdot 6H_2O$), 1 g was dissolved in 5 ml of 12 N HCl aqueous solution and stirred. Then the solution was filtered by filter paper (No. 5C) to remove some insoluble products. A portion of the filtered solution for sampling was concentrated in a reduced pressure desiccator to get a dried product. The dried product in powder was dissolved in 80% by weight isopropyl alcohol aqueous solution. Then the solution containing eluted component was concentrated at reduced pressure in order to remove the solvent and dry. In addition, the procedure consisting of elution, concentration and dry was repeated a few times. Thus crystallized product was prepared.

5% by weight aqueous solution of the crystallized product, 0.01 ml was spotted on a point from 3 cm of the bottom of paper chromatography (PC) filter paper (2 cm × 40 cm), then was developed by n-butyl alcohol : acetic acid : H_20 (5 : 1 : 4, v/v/v) as developing solvent for 15 hours. After developing the filter paper was dried out then colored by spray of 1% by weight potassium ferricyanide aqueous solution as coloring reagent. As a result, it was confirmed that the developed point of the crystallized product was one spot (Rf = 0.07).

In addition, a mixture of $FeCl_2$ and $FeCl_3$ was spotted on a paper chromatography (PC) filter paper as the same way. As a result, it was confirmed that there were two developed points ($FeCl_2$, Rf = 0.095, $FeCl_3$, Rf = 0.36) on the filter paper. These paper chromatography (PC) tests mentioned above accounted for the crystallized product as homogeneous product not mixtures.

Further, a sample solution, 100 ml was prepared by means of dissolving the crystallized product in distilled water. The sample solution (2.5 ml), 0.1% by weight orthophenanthroline aqueous solution (2.5 ml), and sodium acetate-acetic acid buffer solution, pH = 4.5, (25 ml) were put into a mess-flask then distilled water was put into the mess-flask until its marked line. After being allowed to stand for 30 minutes at room temperature, an absorbance (510 nm) of the solution was measured. Ferrous iron in the sample solution was 0.019 g/100 ml calculated from standard curve, obtained by $FeCl_2$ solution in the same way.

Moreover, in the case of putting sample solution into the mess-flask, then hydroxyl mine hydrochloride aqueous solution, 1.0 ml was added to the mess-flask beforehand in order to reduce ferric iron in the sample solution to ferrous iron. As a result, ferrous iron, 0.038 g/100 ml was gotten. It was confirmed that the crystallized product consisted of ferrous iron and ferric iron equivalently because of calculation of ferric iron, 0.019 g/100 ml (= 0.038 g/100 ml - 0.019 g/100 ml). From consideration of the above-mentioned test, it was concluded-that the crystallized product would be $Fe_2Cl_5 \cdot xH_2O$.

[Example 2] (Preparation of ferrous-ferric iron salt)

[0014] Ferric chloride (1.0 mg) was dissolved in 5 ml of 10 N sodium hydroxide aqueous solution and stirred. After stirring, the solution was neutralized with 10 N hydrochloric acid, then was filtered by a filter paper (No.5C) to remove some insoluble products. A portion of the filtered solution for sampling was concentrated in a reduced pressure desiccator to get a dried product. The dried product in powder was dissolved in 80% by weight isopropyl alcohol aqueous solution. Then the solution containing eluted component was concentrated at reduced pressure in order to remove the solvent and dry. In addition, the procedure consisting of elution, concentration and dry was repeated a few times. Thus the crystallized product was prepared. The crystallized product in this example was tested by the same way as Example 1 mentioned above. Thus, it was concluded that the crystallized product would be $Fe_2Cl_5 \cdot xH_2O$.

[Example 3]

[0015] 2 g of ferric-ferrous iron salt prepared in Example 1 was dissolved in 100 ml of a mixture of isopropyl alcohol and water (80:20 weight ratio) and the resulting solution was then added and mixed in kerosene to prepare a fuel modifier No.1 containing 2 ppm of said ferric-ferrous iron salt.

[Example 4]

[0016] 2 g of ferric-ferrous iron salt prepared in Example 2 was dissolved in 100 ml of a mixture of isopropyl alcohol and water (80:20 weight ratio) and the resulting solution was then added and mixed in kerosene to prepare a fuel modifier No.2 containing 2 ppm of said ferric-ferrous iron salt.

[Example 5]

[0017] 5 g of ferric chloride ($FeCl_3$) anhydride was dissolved in 100ml of a mixture of isopropyl alcohol and water (75:25 weight ratio) and the resulting solution was then added and mixed in kerosene to prepare a fuel modifier No.3 containing 3 ppm of ferric chloride.

[Example 6]

[0018] 5 g of ferrous chloride ($FeCl_2$) anhydride was dissolved in 100 ml of a mixture of isopropyl alcohol and water (75:25 weight ratio) and the resulting solution was then added and mixed in kerosene to prepare a fuel modifier No.4 containing 3 ppm of ferrous chloride.

[Efficiency Test]

[0019] Said fuel modifiers No.1, No.2, No.3 and No.4 were respectively added to 1000 ml of gasoline, adding amount of each fuel modifiers being 0.5 ml and driving test using FORD EXPLORER was carried out by using each gasoline modified by each fuel modifier. The results are shown in Table 1.

Table 1

Fuel Modifier	No Additive	No.1	No.2	No.3	No.4
Fuel consumption efficiency km/l (10mode test)	9	10.4	10.4	10.0	10.2

[0020] Referring to Table 1, it is recognized that fuel consumption efficiency is improved to more than 15%.

[0021] The results of the analysis of components contained in the exhaust gas during driving test are shown in Table 2.

Table 2

	HC	CO	CO_2	NOX	CH_4	N-CH_4
Fuel Modifier No.1	0.019	0.312	499	0.068	0.011	0.008
Fuel Modifier No.2	0.018	0.310	498	0.065	0.010	0.008

Table 2 (continued)

	HC	CO	CO_2	NOX	CH_4	N-CH_4
Fuel Modifier No.3	0.020	0.315	499	0.070	0.012	0.010
Fuel Modifier No.4	0.020	0.314	499	0.068	0.011	0.009
No Additive	0.042	0.493	501	0.122	0.018	0.025

[0022] Referring to Table 2, it is recognized that HC and N-CH_4 contents reduce to lower than 50%, CO and CH_4 contents reduce to about 60%, and CO_2 is also recognized to reduce a little. Further, comparing said fuel modifiers No.1 to No.4, it is recognized that ferric-ferrous iron salt has a highest efficiency and then ferrous iron salt and then ferric iron salt in sequence.

Claims

1. A fuel modifier comprising an iron salt.

2. A fuel modifier in accordance with Claim 1, wherein said iron salt is ferric-ferrous iron salt.

3. A fuel modifier in accordance with Claim 1, wherein said iron salt is ferrous iron salt.

4. A fuel modifier in accordance with Claim 1, wherein said iron salt is ferric iron salt.

5. A fuel modifier in accordance with Claim 1, wherein said fuel modifier is prepared by adding and mixing an alcohol solution of said iron salt in a solvent having compatibility with fuel.

6. A fuel modifier in accordance with Claim 5, wherein said iron salt is ferric-ferrous iron salt.

7. A fuel modifier in accordance with Claim 5, wherein said iron salt is ferrous iron salt.

8. A fuel modifier in accordance with Claim 5, wherein said iron salt is ferric iron salt.

9. A fuel modifier in accordance with Claim 5, wherein said solvent is petroleum solvent.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP01/04474

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 C10L1/12, C10L1/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl^7 C10L1/00-C10L11/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Toroku Jitsuyo Shinan Koho	1994-2001
Kokai Jitsuyo Shinan Koho	1971-2001	Jitsuyo Shinan Toroku Koho	1996-2001

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CA (STN), WPI/L (QUESTEL), REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 43-9663, B1 (Kurita Kagaku Kogyo K.K.), 20 April, 1968 (20.04.68), Claims; working examples 1, 2 (Family: none)	1-9
X	JP, 40-4215, B1 (Ferenol Chemicals Limited), 06 March, 1965 (06.03.65), Claims; examples 1 to 11 (Family: none)	1-9
X	JP, 58-40390, A (Chuo Kagaku Kenkyusho K.K.), 09 March, 1983 (09.03.83), Claims; examples 1 to 3 (Family: none)	1-9
X	JP, 59-197492, A (Seiki Kagaku K.K.), 09 November, 1984 (09.11.84), Claims; examples 1 to 3 (Family: none)	1-9

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document but published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 08 June, 2001 (08.06.01)	Date of mailing of the international search report 19 June, 2001 (19.06.01)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP01/04474

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	*Citation of document, with indication, where appropriate, of the relevant passages*	Relevant to claim No.
X	JP, 58-53985, A (World Products K.K.), 30 March, 1983 (30.03.83), Claims (Family: none)	1-9
X	GB, 1544309, A (Ferrous Corporation), 19 April, 1979 (19.04.79), Claims & JP, 54-91503, A & US, 4073626, A	1-9
X Y	JP, 62-45691, A (Toa Netsuken K.K.), Claims; page 2, lower right column (Family: none)	1-4 5-9
X Y	JP, 9-122498, A (Toa Netsuken K.K.), 13 May, 1997 (13.05.97), Claims; Par. No. [0005] (Family: none)	1-4 5-9
X Y	JP, 2-225594, A (Mitsubishi Heavy Ind. Ltd.), 07 September, 1990 (07.09.00), Claims; page 2, upper right column (Family: none)	1-4 5-9
X Y	JP, 1-203497, A (Mitsubishi Heavy Ind. Ltd.), 16 August, 1989 (16.08.89), Claims; page 2, lower left column (Family: none)	1-4 5-9
X Y	JP, 60-64111, A (Mitsubishi Heavy Ind. Ltd.), 12 April, 1985 (12.04.85), Claims; page 4, upper right column (Family: none)	1-4 5-9
X Y	JP, 7-197049, A (Taiho Ind. Co., Ltd.), 01 August, 1995 (01.08.95), Claims; Par. No. [0008] (Family: none)	1-4 5-9
X Y	JP, 53-43706, A (Taiho Ind. Co., Ltd.), 20 April, 1978 (20.04.78), Claims; page 3, upper left column to page 3, upper right column (Family: none)	1-4 5-9
X Y	JP, 53-125410, A (Toray Industries Inc.), 01 November, 1978 (01.11.78), Claims; page 2, upper right column to page 2, lower left column (Family: none)	1-4 5-9
X Y	JP, 7-292373, A (Nippon Petrochemicals Co., Ltd.), 07 November, 1995 (07.11.95), Claims; Par. No. [0011] (Family: none)	1-4 5-9
X Y	JP, 9-302360, A (Kazuko MORIMOTO), 25 November, 1997 (25.11.97), Claims; page 2, upper right column (Family: none)	1-4 5-9

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP01/04474

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP, 9-286994, A (Kiguchi K.K.), 04 November, 1997 (04.11.97), Claims; working example 1 (Family: none)	1-4 5-9
X Y	JP, 2-73889, A (Sanyo Chemical Industries Ltd.), 13 March, 1990 (13.03.90), Claims; working examples 1 to 7 (Family: none)	1-4 5-9
X Y	JP, 1-284588, A (Techno Bio K.K.), 15 November, 1989 (15.11.89), Claims (Family: none)	1-4 5-9
X Y	JP, 60-28494, A (The Lubrizol Corporation), 13 February, 1985 (13.02.95), Claims; page 3, upper left column & CA, 1191833, A	1-4 5-9
X Y	JP, 57-155293, A (Ruhrchemie AG), 25 September, 1982 (25.09.82), Claims & DE, 3044907, A1 & FR, 2495180, A1	1-4 5-9
X Y	WO, 87/00193, A1 (Sparol International APS), 15 January, 1987 (15.01.87), Claims & JP, 62-503173, A & EP, 270682, A1 & US, 4948784, A	1-4 5-9
X Y	US, 5145488, A (Hochest Aktiengesellschaft), 08 September, 1992 (08.09.92), Claims & JP, 3-120237, A & EP, 420034, A1	1-4 5-9
X Y	US, 4568360, A (Compagnie Française de Raffinage), 04 February, 1986 (04.02.86), Claims & JP, 59-172592, A & EP, 112219, A1	1-4 5-9