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(54) Title: ADDITIVES DESIGNED TO IMPROVE FUEL QUALITY IN RECIPROCATING INTERNAL COMBUSTION ENGINES

(57) Abstract

The object of the present patent finds application in the field of fuels and internal combustion piston engines. The additives here considered consist of metallorganic compounds or solutions of metal salts, which, through thermic decomposition during the normal functioning of the engine, are transformed into ionic solids with the hexaoctahedric structure of the spinel, of the inverted spinel with the disordered structures of the spinel or garnet. They facilitate a particular type of fixed-bed hydrogenating catalytic cracking which works through solid-gas surface catalysis inside the combustion chamber during the normal functioning of the engine. These ionic solids perform the dual function of promoting hydrogenating catalytic cracking at low temperature and acting as combustion catalysts at high temperature; both these conditions obtain in the combustion chamber at every explosion.

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Additives designed to improve fuel quality in reciprocating internal combustion engines.

Technical Field

The object of the present Patent can be applied to the field of fuels and internal combustion piston engines.

Background Art

The functioning of piston engines, both ignition and diesel, is based on combustion. Under the broad term of combustion there are actually many chemical reactions that occur and overlap, discharging energy in a way that is apparently chaotic but in fact conditioned by temperature, pressure, the state of the matter, type of fuel, quantity of comburent and, last but not least, the possible presence of positive and negative catalysts.

Combustion is not always perfect, however, and engines tend to detonate and to discharge unburnt gases.

Many improvements have been achieved in recent years in engine studies as well as in chemistry, additives, fuels and afterburning catalysis in order to solve these shortcomings.

In particular, in order to inhibit detonation, metallorganic compounds (lead, manganese, etc.) have been used in relatively large quantities to produce a detonation-inhibiting catalysis. In other words, these compounds reduce the combustion speed in the combustion chamber.

The present state of technical knowledge includes a catalysed chemical process for use in reciprocating internal combustion engines to improve fuel quality, filed as an Italian Patent Application by the applicant for the present Patent on July 4th 1994 with Report No. TS94A000007.

The aforementioned Patent application describes a catalysed chemical process consisting in a particular fixed-bed hydrogenating catalytic cracking process by means of solid-gas surface catalysis taking place within the combustion chamber during the normal running of the engine. This process transforms high-boiling hydrocarbons into low-boiling hydrocarbons with a consequent increase in the octane number. The pressure increase caused by the combustion itself is exploited to split the hydrocarbon molecules. Without the catalysts described in the Patent Application the combustion would cause a detonation.

This cracking process uses as a support for the catalysts the carbon deposits usually found in the combustion chamber and on the inner walls of exhaust pipes.

The catalysts used consist of spinel structured double or mixed metal oxides derived from the thermic decomposition of metallorganic compounds added to fuel. These oxides perform the dual function of promoting low-temperature hydrogenating catalytic cracking and acting as combustion catalysts at high temperature. Both these conditions occur in the combustion chamber at every explosion - low temperature at the beginning of mixture ignition, high temperature as combustion progresses. A part of the oxides, leaving the cylinder together with the exhaust gases, permeates the deposits covering the inner walls of the exhaust pipes, transforming the deposits into a catalytic discharge which further reduces the quantity of unburnt gases.

The precursors of "process catalysts" are metallorganic compounds which on thermic decomposition form spinel-structured double and mixed oxides of iron, cobalt and nickel.

Disclosure of Invention

The purpose of the present invention is to make available to consumers a further series of catalyzers able to exploit the chemical process described in the aforementioned Patent Application No. TS94A000007.

Another purpose is to improve fuel at the moment of combustion, reducing detonation and catalyzing the complete combustion to CO_2 and H_2O.

These and other purposes are achieved by the present invention, which concerns a series of additives to be added to fuels or introduced into the combustion chamber, exploiting the above-mentioned chemical process.

These additives are made up of metal salts in solution or metallorganic compounds that, with the high pressures and temperatures developed in the combustion chamber while the engine is running, through pyrolysis form ionic solids with the hexahoctahedric spinel structure, inverted spinel or disordered spinel structures formed by the double or mixed oxides of the various metals.

As the catalyzers are formed by double or mixed metal oxides, below is a list of metal groups that, in the appropriate proportions, form ionic solids with the hexahoctahedric spinel and sometimes garnet structure (the crystals are obviously real and therefore not perfect). One exception is cobalt which, if used alone, tends to form hexagonal lattices that have less resistance at running temperatures.

1)

aluminium	manganese
20-40	50-80

2)

aluminium	manganese	copper
20-30	60-70	2-10

3)

aluminium	manganese	chrome
20-40	40-70	10-20

4)

aluminium	manganese	chrome	zinc
20-30	40-60	7-15	1-5

5)

aluminium	manganese	molibdenum
20-40	40-70	10-20

6)

aluminium	iron	magnesium
15-25	40-70	15-25

7)

aluminium	cobalt	copper	iron	nickel	titanium
5-10	30-45	1-5	20-35	10-20	5-10

8)

aluminium	cobalt	chrome	iron	magnesium
10-25	25-45	5-20	15-25	10-25

9)

barium	iron
10-20	80-90

10)	bismuth	manganese		
	70-90	10-30		
11)	cerium	cobalt		
	20-30	50-70		
12)	cerium	cobalt	rare cerium earth	
	20-30	55-70	5-15	
13)	yttrium	cobalt	rare yttrium earth	
	15-25	65-85	2-15	
14)	cobalt	yttrium		
	65-85	15-35		
15)	cobalt	iron	lead	
	5-20	5-25	65-75	
16)	cobalt	iron		
	30-70	30-70		
17)	cobalt	iron	vanadium	
	40-65	40-60	2-20	
18)	cobalt	iron	chrome	
	5-40	40-75	2-40	
19)	iron	copper	nickel	chrome
	10-20	3-8	60-85	1-5
20)	cobalt	iron	chrome	wolfram
	30-40	35-65	1-10	1-10
21)	cobalt	platinum		
	20-30	70-80		
22)	cobalt	praseodymium		
	60-70	30-40		
23)	cobalt	samarium		
	60-70	30-40		
24)	cobalt	chrome		
	20-80	20-80		

25)	cobalt	chrome	iron	magnesium
	30-40	5-15	15-25	15-25
26)	copper	iron		
	30-40	60-70		
27)	iron	lithium		
	90-98	2-10		
28)	iron	magnesium		
	75-90	10-25		
29)	iron	strontium		
	85-95	5-15		
30)	iron	manganese		
	55-80	25-45		
31)	iron	silicon		
	90-98	2-8		
32)	iron	nickel		
	60-70	30-40		
33)	iron	molibdenum		
	40-70	25-40		
34)	cobalt	iron	molibdenum	
	40-60	15-30	10-30	
35)	cobalt			
	100			

It makes no difference whether the metals are introduced into the combustion chamber in the form of fuel-soluble metallorganic compounds or salts of the various metals in aqueous solution, in the latter case introduced together with the induction air by means of a nebulizer. Metallorganic compounds are preferable, however.

Each group of metals in the list has its own catalytic properties, but it is possible to mix groups together to obtain compromises between the various reactions.

The quantities of metals contained in the fuel additives vary from 0.5 to 10 grammes per 1,000 litres of fuel.

The attributes of the catalyzers used are:

- they have the properties of magnetic materials;
- excellent resistance to temperatures and pressures and the gas movements occurring in the combustion chamber when the engine is running;
- the ability to form a chemical bond with the carbon in the deposits normally present in the combustion chamber and in exhaust pipes;
- they are effective in very low quantities.

The catalyzers in question have the characteristic of not being poisoned by the presence of water vapour, nitrogen, sulphur, calcium, sodium, potassium, etc. Indeed, these substances seem to facilitate the reactions of the process. The catalyzers are also able to promote the cracking of the hydrocarbons inside the combustion chamber, catalyze the hydrogenation of the olefines (alkenes) produced by the cracking at the expense of the humidity of the comburent air, which is used as H-OH ions, and facilitate the complete combustion of fuel and comburent to CO_2 and H_2O.

As described above, the chemical process for which protection has been requested in Italian Patent Application No. TS94A000007 exploits the coked carbon deposits covering the inside of the combustion chamber (piston head and crown) and the inside of the exhaust pipes. These deposits have a micropore structure with a high specific surface, which makes them an ideal support for "process catalysts".

During the functioning of the engine, that is to say at every explosion, the metal oxides derived from the additives in question are thrown and pressed on to the deposits, penetrate the pores and, since the deposits are almost incandescent, some oxides form a chemical bond with the carbon in the deposits, settling there permanently. The result is a catalytic bed able to promote heterogenous-phase solid/gas reactions.

In view of the fact that metal oxides give rise to bunching, it is extremely important that the quantity of catalyzing oxides is not so great as to obstruct the deposit pores or even form syntherisations. It is thus advisable to add to the fuel additives whose total metal content is less than ten grammes per 1,000 litres of fuel.

In the combustion chamber a process similar to "fixed-bed hydrogenating catalytic cracking" takes place by means of solid-gas surface catalysis.

This cracking reaction occurs at every explosion in a few dozen microseconds between the combustion induction time, or "cool flame moment", when the pressure is high but the temperature is not yet high.

It is at the cool flame moment that, thanks to surface catalysis, the energy flow of combustion is modified. It is at this moment that the high-boiling hydrocarbon molecules are split and transformed into low-boiling molecules.

From this moment occurs the hydrogenation of the alkenes formed during the cracking at the expense of the induction air which is used as H-OH ions.

This system works with all types of piston engines: 2 and 4 stroke, petrol, oil or diesel. Depending on the type of additive or additive mix the following results may be obtained:

1) decrease in polluting exhaust gases (especially particled and HC);

2) significant increase in Octane-Road Number in petrol and oil engines;

3) increase in LIB number in petrol engines;

4) decrease in pre-ignitions (rumbling) in oil and diesel engines;

5) the cetane number in diesel engine fuels is not modified;

6) slight increase in engine power according to the degree of humidity of the induction air and its ionization;

7) with some catalysts the engine is more responsive and flexible if the temperature in the cooling system is 10-15 degrees lower than the running temperature;

8) the stoichiometric fuel-air ratio is modified, the mixture is richer, especially when the engine is cold (only for engines with carburettors);

9) in petrol engines the average running temperature is lower, which allows the fitting of hotter sparking plugs;

10) the lambda probe is not affected by the catalysts;

11) most of the catalytic oxides do not damage the traditional catalytic muffler, but are in synergy with it.

Mode for Carrying Out the Invention

Below are some examples of metal groups usable as catalysts in this invention. It is to be understood that in the examples, a preferred but not exclusive list of possible metal groups, the proportions between the groups are indicative only and do not constitute limits to the present invention:

1)

aluminium	manganese
30	70

2)

aluminium	manganese	copper
28	70	2

3)

aluminium	manganese	chrome
30	60	10

4)

aluminium	manganese	chrome	zinc
28	60	10	2

5)

aluminium	manganese	molibdenum
30	60	10

6)

aluminium	iron	magnesium
18	65	17

7)

aluminium	cobalt	copper	iron	nickel	titanium
8	38	3	29	14	8

8)

aluminium	cobalt	chrome	iron	magnesium
18	35	10	20	17

9)

barium	iron
15	85

10)

bismuth	manganese
80	20

11)	cerium	cobalt		
	34	66		
12)	cerium	cobalt	rare cerium earth	
	25	65	10	
13)	yttrium	cobalt	rare yttrium earth	
	20	75	5	
14)	cobalt	yttrium		
	75	25		
15)	cobalt	iron	lead	
	10	18	72	
16)	cobalt	iron		
	65	35		
17)	cobalt	iron		
	50	50		
18)	cobalt	iron	vanadium	
	49	49	2	
19)	cobalt	iron	chrome	
	33	64	3	
20)	iron	copper	nickel	chrome
	16	5	77	2
21)	cobalt	iron	chrome	wolfram
	36	56	4	4
22)	cobalt	platinum		
	24	76		
23)	cobalt	praseodymium		
	66	34		
24)	cobalt	samarium		
	66	34		
25)	cobalt	chrome		
	60	40		

26) cobalt chrome iron magnesium
50 10 20 20
27) copper iron
34 66
28) iron lithium
95 5
29) iron magnesium
83 17
30) iron strontium
92 8
31) iron manganese
65 35
32) iron silicon
96 4
33) iron nickel
66 34
34) iron molibdenum
65 35
35) cobalt iron molibdenum
60 17 23
36) cobalt
100

The percentage weights of the metals present in the various metal salts or metallorganic compounds that may be used are calculated. On the basis of this result it is possible to calculate the quantities in grammes of compounds or salts to be added to fuel. Example: 1 gramme of lead tetraethyl contains 0.603 grammes of lead, 1 gramme of ironcene contains 0.301 grammes of iron, 1 gramme of aluminium isopropylate contains 0.313 grammes of aluminium; the quantity to be added to fuel varies from 0.5 to 10 grammes of metals per 1,000 litres of fuel.

If it felt that the discharge into the environment of even minimal quantities of ionic solids should be prevented, a permanent-magnet magnetic trap may be fitted to the end of the exhaust pipe. The particles will be intercepted because they are magnetic material.

Claims

1 - Additives designed to improve the quality of fuel for reciprocating internal combustion engines, already described in the Italian Patent Application filed by the same applicant on July 4th 1994, Report No. TS94A000007, consisting in a particular process of fixed-bed hydrogenating catalytic cracking through solid-gas surface catalysis occurring inside the combustion chamber during the normal functioning of the engine; this process transforms high-boiling hydrocarbons into low-boiling hydrocarbons with a consequent increase in the octane number; the cracking process uses as support for the catalysts the carbon deposits usually found inside the combustion chamber and on the inner walls of the exhaust pipes; the additives are characterised by having the properties of magnetic materials and consisting of metallorganic compounds or metal salt solutions which, through thermic decomposition during the normal functioning of the engine, are transformed into ionic solids with hexahoctahedric spinel structure, inverted spinel structure or disordered spinel or garnet structures; these ionic solids perform the dual function of promoting hydrogenating catalytic cracking at low temperature and acting as combustion catalysts at high temperature; both these conditions obtain in the combustion chamber at every explosion; furthermore, a part of these oxides, leaving the cylinder with the exhaust gases, permeates the deposits covering the internal walls of the pipes, thus transforming the pipes into a catalytic exhaust which further reduces the quantity of unburnt gases.

2 - Additives designed to improve fuel quality, according to the previous claim, characterised by the fact that they may be used in extremely limited quantities since, because the metal oxides give rise to bunching, large quantities of catalyzing oxides could obstruct the pores of the deposits or even form syntherizations; the quantities of metals contained in the additives varies from 0.5 to 10 grammes per 1,000 litres of fuel.

3 - Metal catalysts, according to the previous claim, characterised by the

fact that they may be used in groups of metals, provided that they are used in the proportions necessary to form ionic solids with hexahoctahedric spinel structure and sometimes garnet structure, of which a preferential list is shown below:

1)	aluminium	manganese				
	20-40	50-80				
2)	aluminium	manganese	copper			
	20-30	60-70	2-10			
3)	aluminium	manganese	chrome			
	20-40	40-70	10-20			
4)	aluminium	manganese	chrome	zinc		
	20-30	40-60	7-15	1-5		
5)	aluminium	manganese	molibdenum			
	20-40	40-70	10-20			
6)	aluminium	iron	magnesium			
	15-25	40-70	15-25			
7)	aluminium	cobalt	copper	iron	nickel	titanium
	5-10	30-45	1-5	20-35	10-20	5-10
8)	aluminium	cobalt	chrome	iron	magnesium	
	10-25	25-45	5-20	15-25	10-25	
9)	barium	iron				
	10-20	80-90				
10)	bismuth	manganese				
	70-90	10-30				
11)	cerium	cobalt				
	20-30	50-70				
12)	cerium	cobalt	rare cerium earth			
	20-30	55-70	5-15			
13)	yttrium	cobalt	rare yttrium earth			
	15-25	65-85	2-15			

14)	cobalt	yttrium		
	65-85	15-35		
15)	cobalt	iron	lead	
	5-20	5-25	65-75	
16)	cobalt	iron		
	30-70	30-70		
17)	cobalt	iron	vanadium	
	40-65	40-60	2-20	
18)	cobalt	iron	chrome	
	5-40	40-75	2-40	
19)	iron	copper	nickel	chrome
	10-20	3-8	60-85	1-5
20)	cobalt	iron	chrome	wolfram
	30-40	35-65	1-10	1-10
21)	cobalt	platinum		
	20-30	70-80		
22)	cobalt	praseodymium		
	60-70	30-40		
23)	cobalt	samarium		
	60-70	30-40		
24)	cobalt	chrome		
	20-80	20-80		
25)	cobalt	chrome	iron	magnesium
	30-40	5-15	15-25	15-25
26)	copper	iron		
	30-40	60-70		
27)	iron	lithium		
	90-98	2-10		
28)	iron	magnesium		
	75-90	10-25		

29) iron strontium
85-95 5-15
30) iron manganese
55-80 25-45
31) iron silicon
90-98 2-8
32) iron nickel
60-70 30-40
33) iron molibdenum
40-70 25-40
34) cobalt iron molibdenum
40-60 15-30 10-30
35) cobalt
100

these different groups of metals can be mixed together to obtain compromises among the various reactions.

4 - Additives, according to the previous claims, characterised by the fact that they may be introduced into the combustion chamber in the form of fuel-soluble metallorganic compounds and in the form of salts of the various metals in aqueous solution, the latter introduced together with the induction air by means of a nebulizer.

5 - Additives, according to the previous claims, characterised by the fact that the ionic solids used have properties which enable them to remain unaffected by the pressures and temperatures occurring inside the combustion chamber; some of these ionic solids have the property of forming chemical bonds with the carbon of the deposits, thus constituting a basis upon which other oxides will fix; the way in which they are anchored and the great stability of the catalysts make it possible to limit the quantities of metallorganic additives to the minimum required to replace particles of catalyzed deposits which have been mechanically and chemically eroded

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10G47/00 C10L1/10 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)
IPC 6 C10G C10L

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	DE,A,25 02 307 (SYNTEX INC) 31 July 1975 -----	

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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