⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 072 521**
A2

⑫
EUROPEAN PATENT APPLICATION

㉑ Application number: 82107205.5

㉒ Date of filing: 10.08.82

(51) Int. Cl.^{3}: **C 10 L 9/10**
C 10 L 5/10

㉚ Priority: 12.08.81 JP 126101/81

㊸ Date of publication of application:
23.02.83 Bulletin 83/8

(84) Designated Contracting States:
DE GB

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㊹ Solid fuels.

㊼ The present invention relates to solid fuels comprising a carbonaceous fuel and a combustion accelerating agent encapsulated combustible materials. It is possible to improve moistureproof characteristics under high humidity, keeping quality by preventing the variations of combustion accelerating agent on standing and of ignition characteristics.

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SOLID FUELS

The present invention relates to solid fuels which can easily ignite and the ignition characteristics of which do not deteriorate after preservation under high humidity atmosphere.

In recent years, in the aspect of the prevention of petroleum resources, utilization of coal is advocated. Attention is attracted to coal as fuels in place of the petroleum, because the place of production of the coal is distributed widely and resources are rich in comparison with the petroleum. The coal has been used as fuels since olden times and widely for electric power generation and domestic fuel before the petroleum is spreaded. As the reasons why these fuels were replaced by the petroleum, being many reasons, difficulty of ignition and unhandiness are listed. Referring to the domestic fuel, the ignition point of kerosene which is a typical liquid fuel is 300 to 350°C, whereas an ignition point of coal is generally 400 to 600°C, which is higher than that of the petroleum by 200°C, and then difficult to ignite.

In order to settle the above defect of the coal, two methods are proposed; that is, (1) conversion to flowable fuel easy to ignite by liquefaction or gasification, which method has vigorously been studied in recent years, but it is now impracticable and in progressing stage for economical reasons, and (2) using the coal in the state of solid, the ignition characteristics are improved by addition of a combustion accelerating agent such as oxidizing agent.

Further, the solid fuels emit radiation energy more than liquid fuel or gaseous fuel does, and not so dangerous in stock, so that they have a firm demand for domestic cook and heating.

For example, a formed coal is used generally as heating source for fireplace and cooking oven in Europe, and a briquet is used as fuel for heating floor and cooking in Korea. These solid fuels are difficult to ignite as they are. The ignition characteristics are improved by the addition of oxidizing agent of them at high percentage, for example, above twenty or thirty percents. However, these improved fuels absorb moisture to become less ignitible or not ignitible in extreme case under high humidity atmosphere. The high humidity atmosphere means a relative moisture being higher than 60 percents, which commons in summer in Japan.

Solid fuels are deteriloated in ignition characteristics by absorbing morsture to become not ignitible some times. Further, even igniting in part, the ignited fuel gives out a large amount of white or black smoke or goes out. Such a phenomenon is attributed to absorption of the moisture by moisture absorbable materials contained in the solid fuels.

For the sake of the improvement of the absorbability of the solid fuels, several methods are proposed. It is one method that a resin is mixed into solid fuels in a form of liquid or powder. However, this method causes a large amount of unburned materials of the resin to smoke heavily. Further, a method that humidity resistance is given to the solid fuels by the addition of fat or oil is proposed. However, in such a case, extremely large amount of white or black smoke arises as the resin. Particularly when resin or fat is used, a bad smell arises.

Such a problem relating to the usual humidity resistant solid fuels is attributed to a large excess of humidity resistant materials to be added. However, in order to give the humidity resistance to the solid fuels, the large excess of humidity resistant material must be added according to a usual method of humidity resistance based on a macroidea such as addition of or dipping in the humidity resistant materials.

Furthermore, in many times, carbonic materials such as charcoal; wood chip, powder or shavings; or paper are used as the solid fuels, but these materials have moisture-absorbing characteristics from atmosphere at high humidity.

In the meanwhile, a combustion accelerating agent used for the solid fuels includes nitrates, perchromates, permanganates, and oxalates as typical examples, most of which have a high water solubility.

In general, a combustion accelerating agent is used for making ignition of solid fuels easier, accelerating combustion or preventing going-out. The combustion accelerating agent is roughly classified to following three kinds of material:

(1) Easily ignitible organic materials: organic materials having low ignition point such as alcohols, hydrocarbons, amines, fatty acids and salts of fatty acid.

(2) Oxidizing agents: materials accelerating oxidation of carbonic materials such as coal and charcoal, and improving ignition characteristics and combustion characteristics, for example, nitrates, perchlorates, chlorates, permanganates, dichromates and chromates of alkaline metals or alkaline earth metals.

(3) Catalyst: catalyst for accelerating the oxidation of carbonic materials such as manganese dioxide.

If the solid fuels containing above combustion accelerating agent is held under a high humidity condition, the combustion accelerating agent which is a moisture-absorbable absorbes moisture in atmosphere, in which a part of water soluble material in the solid fuels is dissolved. Repeating such processes again and again, the moisture is absorbed more and more to deteriolate the ignition characteristics of the solid fuels extremely.

Examples of usual solid fuels using a humidity resistant material as references hereinafter.

Reference Example 1 of usual solid fuel:

paraffin	9 percent by weight
sodium nitrate	2 percent by weight
ferrosilicon	2 percent by weight
mashed paper	3 percent by weight

Though this composition can easily ignite by a piece of match, it gives out a large amount of white or black smoke.

Reference Example 2 of usual solid fuel:

charcoal	20 percent by weight
smokeless coal	10 percent by weight
nitro cellulose	1 percent by weight
polyvinyl alcohol	1 percent by weight
potassium dichromate	2 percent by weight

This composition is inferior to the composition of the above Reference Example 1 in the ignition characteristics, and moreover it gives out white smoke during combustion. In addition, it does not ignite in the humidity resistance test as described hereinafter.

An object of the present invention is to improve the aforementioned problems, which is based on treatment for humidity resistance according to microidea but not macroidea.

In the solid fuels ability of the ignition is depended on whether the combustion accelerator therein plays a role successfully.

According to the present invention, the combustion accelerating agent is microencapsulated with combustible materials having a water repellency or waterproofness to give solid fuels improved in the humidity resistance so that the above problems in the usual humidity resistant igniting agent are solved. Following effects are obtained:

(1) As humidity resistant materials are used mainly to combustion accelerating agent, they act efficiently to the accelerating agent, and even at high humidity the combustion accelerating agent is active equally to at dry atmosphere. Therefore, the humidity resistance of solid fuels is improved.

(2) According to the present invention, the white or the black smoke in the usual solid fuels and bad smell are reduced remarkably, and the amount of the humidity resistant materials are lowered.

The carbonic materials of the present invention include coal and charcoal as a main component and they may be combined with other materials such as coke, activated carbon, carbon black, wood piece and paper.

The combustion accelerating agent of the present invention includes metal compounds such as nitrates, perchlorates, chlorates, dichromates chromates, permanganates, oxalated carbonates and hydroxides of alkaline metals or alkaline earth metals salt; organic solvent such as methanol,

ethanol, propanol, benzene, toluene, xylene, petroleum ether, hexamethylenetetramine, ethylenediamine, and triethylamine; iron family metals compounds such as nitrates, sulfates, chlorides, oxalates, carbonates, oxides of iron, cobalt, nickel and the like.

In the above alkaline metal salts and alkaline earth metal salts, chlorates and oxalates are poison and the chlorates are dangerous for explosion. Therefore, they must be handled with sufficient care. Besides, perchlorates have the nearly same properties as those of chlorates, while not so dangerous, and burn with a spark as fireworks, which is also dangerous. Dichromates and chromates which include chromium are poisonous materials. Nitrates give out white smoke including alkaline materials, which corrode metals and are poisonous for livings.

Though, as aforementioned, oxidizing agents have peculiar defects severally, nitrates are more desirable to be used because of their mild activity and explosion characteristics in comparison with chlorates, perchlorates, permanganates, and oxalates which are dangerous for explosion and poisonous. Anyway, it is important that the oxidizing agents to be used are minimized. As usual easily ignitible solid fuels are composed with the consideration of safety in use under dry condition, the oxidizing agent is minimized to amount required at dry condition. Accordingly, under a high humidity, these solid fuels become not only extremely less ignitible and lower in a combustion rate but also in extreme case not ignitible.

In the meanwhile, the solid fuels according to the present invention, in which the oxidizing agents are microencapsulated, can maintain the ignition characteristics at dry even under high humidity condition by the microencapsulation of the oxidizing agents. In addition, as the combustible organic materials are burned in flames, evacuated unburned gas containing carbon monoxide, aldehydes, hydrocarbon such as methane and the like which cause very serious problem in the usual solid fuels is perfectly oxidized so that the evacuated gas characteristics are also improved.

The iron family metal compounds include chlorides, nitrates, sulfates, oxalates, carbonates, acetates and oxides of iron, cobalt or nickel. The ignition points of main components of solid fuels such as coal, coke, graphite and the like, which are about 400 to 600°C, are lowered by the addition of a small amount of the iron family metal salts by 100 to 150°C, so that the solid fuels become more ignitible. Thus, the addition can reduce the amount of the oxidizing agents used for the improvement of ignition of solid fuels so as to reduce the poisonous gas such as NO_x given out by decomposition of the oxidizing agents. However, as the most iron family metal salts are moisture absorbable materials, the untreated metal salts become not only extremely less ignitible but also not ignitible under high humidity.

In the present invention, the moisture absorbance is protected from moisture absorption even under the high humidity by microencapsulation of the iron family metal salts, and the combustible microcapsule melts to burn at the same time of the combustion of the solid fuels, so that the metal salts can act with the same activity as the initial state. The results are excellent.

In the meanwhile, if organic solvents which are easily ignitable materials can be used for the solid fuels, the ignition characteristics will be improved. However, the most of organic solvent are volatile and volatilize on standing, so that they can not be used as a component of the solid fuels as they are.

According to the present invention, the volatilization of the organic solvents can be prevented by microencapsulation thereof, and the ignition characteristics are maintained without any change on standing.

When the solid fuels burn, the capsule melts and the organic solvent volatilizes to burn in flames.

Further, hydrides such as sodium boron hydride is decomposed to give out hydrogen gas. Therefore, if the hydrides can be applied to the solid fuels in small amount, they can burn in mild flames. However, the hydrides are liable to be decomposed easily by moisture in atmosphere to become not usable in general. According to the present invention the hydride can be shielded against the atmosphere so as to be used as a combustion accelerating agent of the solid fuels. The resultant fuels have excellent properties.

As aforementioned the ignition characteristics can be improved by the microencapsulation of the combustion accelerating agent for the solid fuels.

Additionally the humidity resistance characteristics of the solid fuels are improved moreover by the microencapsulation of the moisture absorbable materials in the solid fuels as well as it becomes possible to produce solid fuels which do not make hands dirty with carbonic materials when they are picked up contrary to usual solid fuels including the moisture absorbable materials.

According to the present invention, the microcapsule is a vessel, a package, or a container having a microscopic size such as about 5 to 300μ in general and surrounded by polymer cell, in which fine particles of materials are contained.

General examples in which microcapsule is utilized include applications to pressure sensitive carbon paper, drug, perfume, oil capsule and the like. There are exemplified microcapsule of leuco dye with acacia and gelatin in the carbon paper, microcapsule of aspirin with ethyl cellulose in drug, microcapsule of menthol of tabacco in perfume, and microcapsule of gun oil or lubricant with alginic acid in oil capsule respectively.

In the present invention combustible materials having water repellency or waterproofness are used as film forming materials for microcapsule. The combustible materials include hydrocarbon polymer such as polyethylene, polypropylene, polystyrene, and resins such as silicone resin, polyvinyl acetate, epoxy resin, polymethyl methacrylate, polyamide resin, acrylonitrile-vinylidene chloride copolymer, polyvinyl formal, ethyl cellulose, nitrocellulose, gelatine and acacia.

The microencapsulation includes chemical, physical-chemical and mechanical or physical method roughly. There are exemplified an interfacial polymerization as the chemical method, a phase-separation from aqueous solution or organic solvent as the physical-chemical method and a spray drying as mechanical or physical method.

In the present invention, the microencapsulation does not restricted to the above exemplified methods.

Several kinds of method for producing the solid fuels of the present invention are exemplified without restriction. One of the examples is the method in which mixture of carbonic materials (coal, charcoal and the like), microencapsulated combustion accelerating agent (potassium nitrate, calcium nitrate and the like) and binding materials are mixed and formed to a desirable shape followed by dried to give the solid fuels. In the production of the solid fuels, metal powders such as aluminium and metal silicon, and forming auxiliaries such as clay for example bentonite may be added if desired. As the binding materials, molasses, carboxymethyl cellulose, tar, pitch, waste liquor of pulp and the like may be used in the present invention.

The present invention is illustrated according to Examples hereinafter. In the Examples humidistat is prepared according to JIS Z8806 in order to make the experimental conditions uniform under the high humidity atmosphere. That is, the saturated aqueous solution of calcium nitrate tetrahydrate and potassium chromate are added into desiccators separately, in which the former makes humidistat of relative humidity of 55 percent and the latter makes that of relative humidity of 88 percent. Using this humidistat combustible characteristics of the solid fuels composed with following formulations are experimented under a high humidity atmosphere.

Example 1

Potassium nitrate is added to polyvinyl acetate solution (10% by weight) in methyl ethyl ketone and dispersed sufficiently and then n-hexan is added. The mixture is mixed at room temperature for one hour and held for 12 hours at 0°C. Then, solid is separated, rinsed with cold n-hexan (about 4°C), and dried to give microencapsulated potassium nitrate.

Accroding to a similar process to the above, potassium permanganate is also microencapsulated. Using these microencapsulated potassium nitrate and potassium permanganate solid fuels are prepared with following formulation:

Formulation

charcoal	40% by weight
smokeless coal	10% by weight
KNO_3	15% by weight

$KMnO_4$	2% by weight
adhesive agent	2% by weight

Example 2

Eight solid fuels are prepared according to Example 1 excepting that the microencapsulating agent is replaced by followings:

Solid fuel 2: polyethylene
Solid fuel 3: polypropylene
Solid fuel 4: polystyrene
Solid fuel 5: silicone resin
Solid fuel 6: epoxy resin
Solid fuel 7: polymetyl methacrylate
Solid fuel 8: polyamide
Solid fuel 9: acrylonitrile-vinylidene chloride copolymer.

Example 3

According to the Example 1, ferric chloride, ferric nitrate and potassium nitrate are microencapsulated with polyvinyl acetate. Using the resultant microcapsules solid fuels 10 and 11 are prepared. The formulations of the solid fuels are as follows:

Formulation of solid fuel 10

smokeless coal	50%	by weight
KNO_3	15%	"
$FeCl_3$	1%	"
binding material	2%	"

Formulation of solid fuel 11

smokeless coal	50%	by weight
KNO_3	15%	"
$Fe(NO_3)_3$	1%	"
binding material	2%	"

Example 4

Sodium boron hydride is added to polystyrene solution (10% by weight) in xylene and treated in the same manner as Example 1 to give a microencapsulated sodium boron hydride, two parts by weight of which are added to the solid fuel of the Example 1 to prepare solid fuel 12.

As comparative examples, solid fuels 13, 14 and 15 are prepared, in which the solid fuel 13 is prepared in the same formulation as Example 1 excepting that the potassium nitrate and potassium permanganate are not microencapsulated, solid fuel 14 is prepared in the same formulation of Example 4 excepting that the sodium boron hydride, potassium nitrate and potassium permanganate are not microencapsulated and solid fuel 15 is prepared by the same formulation of the solid fuel 10 of the Example 3 excepting that the ferric chloride is not microencapsulated.

These solid fuels are held in the above humidistat at room temperature for 24 hours. These fuels are picked out from the himidistat and ignited immediately by match and estimated for several items. The results are shown in Tables 1 and 2, in which the former includes the results from the holding under relative himidity of 55% and the latter indicates results from relative humidity of 88%.

In Tables the evaluations are shown by following marks:

(1) Ignition characteristics by match

A: ignited by one piece of match

B: ignited by two pieces of match

C: ignited by three or more than three pieces of match

(2) White smoke

A: small amount

B: middle

C: large amount

(3) Spread of combustion

A: continuous

B: intermittent

C: end in smoke

(4) Crack during combustion

A: not found

B: found

(5) Spark

A: small amount

B: middle

C: large amount

(6) Smell

A: scarcely

B: a little

C: bad

Table 1

solid fuels	ignition by match	white smoke	spread of combustion	sprit	spark	smell	synthetic estimation
1	A	A	A	A	A	A	A
2	A	A	A	A	A	A	A
3	A	A	A	A	A	A	A
4	A	A	A	A	A	A	A
5	A	A	A	A	A	A	A
6	A	A	A	A	A	A	A
7	A	A	A	A	A	A	A
8	A	A	A	A	A	A	A
9	A	A	A	A	A	A	A
10	A	A	A	A	A	A	A
11	A	A	A	A	A	A	A
12	A	A	A	A	A	A	A
13	B	B	B	A	A	B	B
14	B	B	B	A	A	B	B
15	A	A	A	A	A	A	A

Table 2

solid fuels	ignition by match	white smoke	spread of combustion	sprit	spark	smell	synthetic estimation
1	A	A	A	A	A	A	A
2	A	A	A	A	A	A	A
3	A	A	A	A	A	A	A
4	A	A	A	A	A	A	A
5	A	A	A	A	A	A	A
6	A	A	A	A	A	A	A
7	A	A	A	A	A	A	A
8	A	A	A	A	A	A	A
9	A	A	A	A	A	A	A
10	A	A	A	A	A	A	A
11	A	A	A	A	A	A	A
12	A	A	A	A	A	A	A
13	C	-	C	-	-	-	C
14	C	-	C	-	-	-	C
15	C	-	C	-	-	-	C

Note: Solid fuels 13, 14 and 15 do not ignite.

In the meanwhile, solid fuels prepared using microencapsulated oxalates, perchlorates or dichromates as a combustion accelerator give the same excellent effects as the results of the aforementioned solid fuels 1 to 12 in the humidity resistance test. Further, when benzyl cellulose or nitrocellulose is used as a microencapsulating agent for humidity resistant treatment, they give the same excellent effects as methyl cellulose gives.

Though microencapsulation of the above Examples are one produced by physical-chemical treatments, the microencapsulation for the humidity resistance treatment is not restricted to the above treatments, but microencapsulation according to chemical or physical method may be used and, of course, the resultant solid fuels having the same effects as those from the above physical-chemical method can be obtained.

As apparent from the Tables 1 and 2, the solid fuels 1 to 12 which include the microencapsulated combustion accelerating agent are improved remarkably in the humidity resistance in comparison with the solid fuels 13 and 15 in which the combustion accelerating agent is not microencapsulated.

Reasons for the above are considered that the inhelent ability of the combustion accelerating agent is maintained, even in high humidity atmosphere, as in dry condition by the protection or the shield of the accelerating agent from moisture of exterior by the microencapsulation with a combustible materials having a water repellency or a waterproofness, and at combustion the capsule is melted and decomposed so that the combustion accelerating agent can act sufficiently.

As the cell materials of the microcapsule used in the solid fuels 1 to 12 burn as gasifying, the fuels are burned in mild flames whereas the solid fuels 13 and 15 burn without flames.

As aforementioned the amount of the resin to be used is too much in usual humidity resistance treatment.

For example, it amounts to 56% by weight of total amount of the solid fuel so that the large amount of combustible gas is given out. A part of the gas can not be burned to be given out without decomposition which causes white smoke. According to the present invention, as the amount of the cell materials of the microcapsule to be used is a little, that is, generally less than about 5% by weight of the solid fuels, gas is given out in suitable amount to burn in flames without smoke, which is desirable for solid fuels.

What is claimed is:

1. Solid fuels comprising a microencapsulated combustion accelerating agent.

2. The solid fuels according to Claim 1 in which the combustion accelerating agent is microencapsulated with a water repellent or waterproof combustible material.

3. The solid fuels according to Claim 1 in which the combustion accelerating agent is selected from the group consisting of nitrates, dichromates, chlorates, oxalates, carbonates, hydrides and oxides of alkaline metals or alkaline earth metals; nitrates, sulfates, chlorides, carbonates and oxides of iron family metals; and organic solvents.

4. The solid fuels according to Claim 2 in which the combustible material is selected from the group consisting of polyethylene, polypropylene, polystyrene, silicone resin, polyvinylacetate, epoxy resin, polymethyl methacrylate, polyamide resin, acrylonitrile-vinylidene chloride copolymer, acrylonitrile-styrene copolymer, polyvinyl formal, ethyl cellulose, benzyl cellulose, nitrocellulose, gelatine and acacia.

5. Solid fuels according to Claim 3 in which the iron family metals are selected from the group consisting of iron, nickel and cobalt.

6. The solid fuels according to Claim 3 in which the organic solvent is selected from the group consisting of methanol, ethanol, propanol, benzene, toluene, xylene, petroleum ether, hexamethylenetetramine, ethylenediamine,

triethylamine.

7. The solid fuels according to Claim 3 in which alkaline metals are selected from the group consisting of lithium, sodium and potassium.

8. The solid fuels according to Claim 3 in which the alkaline earth metals are selected from the group consisting of calcium, strontium and barium.