Patented June 30, 1936 2,046,209

UNITED STATES PATENT OFFICE

2,046,209

PROCESS OF PRODUCING SOLIDIFIED FUEL

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No Drawing. Application February 24, 1934, Serial No. 712,805

12 Claims. (Cl. 44—7)

The present invention relates to combustible gels or solid fuels, and more especially it concerns the production of a novel, solidified fuel in which a liquid, combustible component is maintained as a firm, stable, homogeneous gel by a supporting framework of a colloidal, inorganic substance such as colloidal silicic acid, silica, titanic acid, and the like.

Many solidified fuels having alcohols as their combustible constituent are now well known. Such fuels frequently contain various soaps or soap-making ingredients as the solidifying or bodying agent, with or without additional combustible or non-combustible fillers. These solidified fuels utilizing a soap base possess in considerable degree the objectionable property of liquefying when heated, particularly while the liquid combustible is burning at the surface of the solid mass. The presence of the exuded liquid increases the difficulties attendant the safe handling of the solid fuel.

Other well known solid fuels in present use utilize nitrocellulose as the solidifying agent. Although such fuels remain solid during combustion, they tend to burn with a pulsating, non-uniform flame, due to minute explosions that occur as the nitrocellulose particles are exposed at the surface of the fuel and burn unevenly. These fuels also exude a relatively large volume of liquid upon standing, which is very objectionable from the standpoint of safety and limits their effective utility.

The present invention is based upon the discovery that stable gels of various combustible liquids can be prepared by the use of small amounts of organic derivatives of inorganic elements such as silicon and titanium,—particularly the esters of silicic acid,—and that these stable gels are tough and elastic, and tenaciously retain the combustible within the gel body, so that the gels burn uniformly at the ignited surface without substantial or observable liquefaction.

Among the more important objects of the invention are: to provide in novel manner for the production of a solidified fuel which will burn without substantial separation of a liquid combustible to form a separate liquid phase; to provide a novel solidified fuel having a low content of solids and which burns substantially without liquefaction of any component thereof; and to provide a novel, homogeneous, solidified fuel which can be quickly and readily prepared, and which is highly resistant to deterioration by ageing. These and other objects will be apparant from a review of the following description and claims.

In its broadest scope the invention includes the preparation of stable gels containing one or more liquid combustibles,—and particularly those which are in some degree miscible with water or other hydrolyzing agent. Among such liquids that have been gelled may be mentioned methanol, ethanol, isopropanol, and ketones such as acetone.

In the practice of the invention, the liquid combustible is mixed with an ester or other organic derivative of an inorganic acid, such as the various esters of silicic acid capable of producing and uniformly distributing throughout the combustible liquid a relatively stiff framework or body of inorganic substance. The ester or compound is then hydrolyzed by water originally present in the mixture or that added for the purpose, and after some time the entire mass sets to a stable firm gel. This gel tenaciously retains the liquid combustible dispersed therethrough during subsequent transportation and storage, while allowing the ready combustion of the liquid at the surface of the gel upon its ignition, but restraining such free escape of the liquid at the said surface as to produce partial separation of the liquid combustible to form a liquid phase during burning or upon subsequent cooling of the unburned solidified fuel. A small amount of alkali or acid, preferably the former, accelerates the gellation.

Water in excess of that required for hydrolysis may be present in the gel; and this often is desirable in some instances for reducing or eliminating soot formation during combustion of the gel.

Among the esters of orthosilicic acid which have been found particularly useful as a gelling agent are the monohydric alcohol silicates such as tetra-methyl silicate and tetraethyl silicate; the condensed monohydric alcohol silicates such as methyl and ethyl disilicates, and methyl trisilicate; and the polyhydric alcohol silicates such as primary, secondary and tertiary glycerol silicates, the primary and secondary ethylene glycol silicates; and the condensed polyhydric alcohol silicates.

The conditions under which the various esters give good gels will vary somewhat, depending upon the ester used and the liquid gelled. Generally, tetra-methyl orthosilicate and ethylene glycol orthosilicate hydrolyzes more readily than tetraethyl orthosilicate, and therefore may produce gels more quickly.

In the preparation of solidified fuel gels of methanol, ethanol or isopropanol, a preferred procedure is to thoroughly incorporate a small amount of the ester or of a solution of the ester in a volatile solvent,—generally around 3 to 10% of the ester by volume,—with the liquid combustible containing approximately 5 to 15% of water and preferably made alkaline by a trace of caustic soda or other alkali. The hydrolysis of the ester and the agglutination of the colloidal silicic acid or silica is accelerated in the presence of a small amount of an alkali; and the firm, permanent gel forms in a reasonably short time at normal room temperatures, though lower or higher temperatures can be used. Gellation occurs in from a few minutes to several days, depending upon the liquids used and the proportions of the substances present, all of which conditions can be substantially varied. The time required for gellation may be shortened by moderate heating for a short time.

For purposes of illustration only, the following example is given: a mixture of 85 c. c. ethanol, 2 c. c. water, and .02 gram of caustic soda in a 20% aqueous solution had intimately mixed therewith 5 c. c. of methyl orthosilicate, $Si(OCH_3)_4$. Forty-eight hours were required for completion of gellation to yield a solidified fuel having good fuel value and physical structure, and from which the liquid did not exude in other than traces.

By increasing the amount of alkali in the above example to .2 gram, the time required for gellation was reduced to a half hour.

While tetra-methyl orthosilicate, containing 38% to 39% SiO_2, has given particularly good results with alcohols, a solution of glycol silicate ($Si(O_2C_2H_4)_2$) in ethanol, the said silicate containing 22% to 25% SiO_2, gives excellent results with ketones as well as with alcohols. Tetraethyl orthosilicate and the condensed ethyl silicates (39% SiO_2) hydrolyze and set more slowly than the others.

The combustible gels produced in accordance with this invention can be produced in somewhat brittle form, so that they can be broken into pieces by a suitable blow or impact. They readily may be prepared in granular or powder form in the usual impact mills or the equivalent. The extent of such brittleness may be controlled, being generally proportional to the amount of the ester used in the preparation of the gel. The brittleness also can be reduced by increasing the amount of water in the mixture to be gelled. For instance, one ethanol gel containing 10% of water and 5% of methyl orthosilicate is fairly elastic, and is still intact after fifteen months of handling in demonstration.

The normal tendency for a gel to exude liquid upon standing is controlled and minimized in the present invention by the regulation of the alkali, and/or by the regulation of the water present. Increase of water apparently reduces the syneresis of the gel as well as decreases the degree of brittleness.

The silica, or its equivalent, formed by the hydrolysis of the corresponding ester, and the trace of alkali added in some cases, are the only solid constituents present in these gels. Very satisfactory gels contain around 2% by weight of silica (SiO_2). As the amount of ester is increased to give a higher content of silica or its equivalent, harder gels are produced, of increasing brittleness. On the other hand, when the amount of the ester used is much less than that required to provide a gel of around 1.7% silica content, the gels formed are quite soft.

All of the gels burn freely without any liquefaction or separation whatever of their components. A can of the gelled liquid combustible can be ignited, extinguished, and reignited, until all of the gel is burned, and only the small amount of silica present in the gel remains in the can as a white sand.

The methanol and ethanol gels are excellent solidified fuels, burning with a blue, practically sootless flame. The addition of small amounts of water to the ethanol reduces or eliminates any soot-depositing tendency.

In the case of the high calorific liquid combustibles having a proportion of three carbon atoms or more to each oxygen atom, this carbon content is high enough to effect some carbon deposition during normal combustion. Such gels, however, may be useful in certain cases where high heating value is essential. Carbon deposition may be reduced or prevented by the appropriate introduction of secondary air during combustion.

By effecting the setting of the gels in specially designed containers the solidified fuel can be produced in any desired shape and size to facilitate its subsequent handling, and its ignition and combustion, either within the container or after removal therefrom. In some cases the fuel may be granulated or comminuted.

The invention is adapted for the preparation of solid gels from organic liquids that are miscible in some degree with water or other hydrolyzing agent and with the esters employed, or which may be rendered miscible by suitable treatment.

While I have now fully described the principle of my invention and a particular embodiment thereof which is merely illustrative of the invention, it is to be understood that various modifications of the invention may be made within the scope of the appended claims.

I claim:

1. The process of making a solidified fuel, which comprises intimately mixing together a volatile liquid combustible miscible with a hydrolyzing agent, and a small amount of an aqueous hydrolyzing agent, and adding to the resultant mixture a small amount of an ester of an inorganic acid capable of forming upon hydrolysis and subsequent ignition a refractory oxide, thereby at least partially hydrolyzing the said ester and forming a firm, stable, solidified gel.

2. The process of making a solidified fuel gel, which comprises intimately mixing together an aqueous hydrolyzing agent, and a volatile liquid combustible miscible therewith, and adding to the resultant mixture a small amount of an ester of a silicic acid, thereby at least partially hydrolyzing the latter and forming a stable, solidified, fuel gel.

3. The process of making a solidified fuel gel, which comprises intimately mixing together an alcohol and a small amount of water rendered slightly alkaline by a caustic alkali, and adding to the resultant mixture a small amount of an ester of a silicic acid, thereby at least partially hydrolyzing the latter and forming a stable, solidified, fuel gel.

4. The process of making a solidified fuel gel, which comprises intimately mixing together ethanol and a small amount of water rendered slightly alkaline by a caustic alkali, and adding to the resultant mixture a small amount of an ester of orthosilicic acid, thereby partially hy-

drolyzing the latter to form a stable, solidified fuel gel.

5. The process of making a solidified fuel, which comprises intimately mixing with an alcohol miscible with water a small amount of water rendered slightly alkaline by caustic alkali, and adding to the resultant mixture an ester of an inorganic acid capable of forming upon hydrolysis and subsequent ignition a refractory oxide, thereby at least partially hydrolyzing the ester and forming a stable solidified fuel gel.

6. The process of making a solidified fuel, which comprises intimately mixing with an alcohol miscible with water a small amount of water rendered slightly alkaline by caustic alkali, and adding to the resultant mixture an ester of an inorganic acid capable of forming upon hydrolysis and subsequent ignition a refractory oxide, thereby at least partially hydrolyzing the ester and forming a stable solidified fuel gel, and giving the gel a preselected shape during its formation.

7. The process of making a solidified fuel, which comprises intimately mixing a water-miscible volatile combustible liquid with a small amount of an alkaline hydrolyzing agent, and adding to the resultant mixture around 3% to 10% by volume of an ester of a silicic acid, thereby at least partially hydrolyzing the latter and forming a stable solidified fuel gel.

8. The process of making a solidified fuel, which comprises intimately mixing an alcohol with approximately 5% to 15% of water rendered slightly alkaline by a caustic alkali, and adding to the resultant mixture around 3% to 10% by volume of an ester of a silicic acid, thereby at least partially hydrolyzing the latter and forming a stable, solidified, fuel gel.

9. The process of making a solidified fuel, which comprises intimately mixing with an alcohol miscible with water a small amount of water rendered slightly alkaline by caustic alkali, and adding to the resultant mixture an ester of an inorganic acid capable of forming upon hydrolysis and subsequent ignition a refractory oxide, thereby at least partially hydrolyzing the ester and forming a stable, solidified, fuel gel, and granulating the resultant gel.

10. In the process of making a brittle solidified fuel gel from a mixture of a volatile combustible liquid and an ester of silicic acid by the at least partial hydrolysis of the latter with an aqueous hydrolyzing agent in the presence of the said liquid, the step of adjusting the amount of hydrolyzing agent in the said mixture, thereby regulating the brittleness of the resultant solidified fuel, and the syneresis of the gel.

11. In the process of making a brittle solidified fuel from a mixture of a volatile combustible liquid and an ester of silicic acid by the at least partial hydrolysis of the latter with an aqueous hydrolyzing agent in the presence of the said liquid, the step of adjusting the amount of the said ester present in the mixture, thereby controlling the brittleness of the resultant solidified fuel.

12. The process of making a solidified fuel gel, which comprises intimately mixing an aqueous hydrolyzing agent and a volatile liquid combustible miscible therewith, and adding to the resultant mixture an ester of a silicic acid, thereby at least partially hydrolyzing the latter and forming a stable solidified fuel gel, the said ester being used in amount sufficient to produce a fuel gel having a low silica content of at least 1.7%.

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CERTIFICATE OF CORRECTION.

Patent No. 2,046,209. June 30, 1936.

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It is hereby certified that the above numbered patent was erroneously issued to Carbide and Carbon Chemicals Corporation, whereas said patent should have been issued to Union Carbide and Carbon Corporation, a corporation of New York, assignee by mesne assignments, as shown by the records of assignments in this office; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 22nd day of September, A. D. 1936.

Henry Van Arsdale

(Seal) Acting Commissioner of Patents.

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