United States Patent

Castellucci et al.

[15] **3,661,497**

[45] **May 9, 1972**

[54] **PROCESS FOR BURNING A COMBUSTIBLE LIQUID USING CELLULAR CERAMIC NODULES**

[72] Inventors: **Nicholas T. Castellucci,** 6901 Alcama Dr.; **Ned C. Krouskop,** 611 Pennwood Dr., both of Pittsburgh, Pa. 15235

[22] Filed: **June 2, 1969**

[21] Appl. No.: **829,746**

[52] **U.S. Cl.** **431/7,** 431/326

[51] **Int. Cl.** **F23d 3/18**

[58] **Field of Search** 431/7, 2, 4, 170, 326, 331, 431/356, 298

[56] **References Cited**

UNITED STATES PATENTS

370,883	10/1887	Moore	431/4
405,786	6/1889	Ludde	431/298
755,376	3/1904	Lucke	431/7
1,149,870	8/1915	Thompson, Jr.	431/4
2,246,346	6/1941	Carroll	431/298
3,354,024	11/1967	D'Eustachio et al	161/168
3,556,698	1/1971	Tully et al	431/2

Primary Examiner—Frederick L. Matteson
Assistant Examiner—W. C. Anderson
Attorney—Stanley J. Price, Jr.

[57] **ABSTRACT**

A process for the substantially complete combustion of a layer of combustible liquid floating on a body of water comprising spreading a layer of substantially spherical ceramic nodules on the upper free surface of the layer of combustible liquid. The nodules are wetted with the combustible liquid and the combustible liquid is ignited on the upper surface of the nodules until combustion is self-sustaining. The combustible liquid on the upper surface of the nodules consumed by combustion is continually replaced with combustible liquid from the layer until substantially all of the combustible liquid in the layer is consumed. The cellular ceramic nodules have a multiplicity of separate closed cells and the outer surface of the nodules has a plurality of cup shaped recess portions.

14 Claims, No Drawings

PROCESS FOR BURNING A COMBUSTIBLE LIQUID USING CELLULAR CERAMIC NODULES

CROSS REFERENCE TO RELATED APPLICATIONS

U. S. Pat. No. 3,493,218 entitled "Tower Packing Elements" discloses cellular ceramic nodules with an external surface having a plurality of cup shaped recessed portions.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for the burning of a combustible liquid and more particularly to a process for the complete combustion of a layer of combustible liquid floating on a body of water.

2. Description of the Prior Art

During the transfer of liquid fuel from one vessel to another, either at sea or on other navigable waters, discharge of combustible hydrocarbon liquids or other pollutants onto the water often occurs. Similarly, accidents in the production and transportation of petroleum products, such as weld blowouts and pipeline leaks, cause major water pollution problems. Such accidents and other catastrophes, such as the sinking or damaging of an ocean going or river transportation vessel, cause water pollution problems that are often unsolvable or that are remedial only at exorbitant expense. The possibility of such incidents of water pollution and contamination of adjacent land areas has severely restricted the recovery of large amounts of petroleum from off-shore reservoirs.

An inexpensive solution would be the combustion of the layer of pollutant liquid from the surface of the water. This solution, however, has not been found feasible for many reasons. For example, many hydrocarbon liquids and other pollutant liquids are not readily ignitable. Furthermore, in many instances in which ignition can be obtained, it is not possible to sustain combustion long enough or at sufficiently high temperatures, to consume the pollutant liquid.

Even when dealing with liquids that ordinarily are readily ignitable and relatively combustible, the presence of a relatively thin layer of such liquid underlain by a large body of water produces a physical system in which ignition can not be obtained or in which combustion can not be sustained at all or can not be sustained at sufficiently high temperatures to effect removal of the pollutant liquid. These problems generally arise from the rapid transfer of heat into the underlying body of water and away from the combustible liquid.

Several other solutions to the pollution problem have been suggested in the prior art. It has been suggested that the pollutant be confined with a ring of trash booms or similar devices and then scooped from the water's surface. That solution has been proved to be exorbitantly time consuming and expensive and not completely effective.

Attempts have also been made to absorb the pollutant liquid in straw or other absorbent material which is subsequently transported from the scene and destroyed. That solution has also proved too expensive, time consuming and not entirely satisfactory.

In reference to the combustion of the liquid on the surface of the water, attempts have been made to burn away the pollutant liquid through the use of various igniters or combustion catalysts. This method has proved unsatisfactory because of the inherent expense and the inability to completely consume and remove the pollutant liquid.

Another proposed solution to the problem comprises covering the surface of the pollutant liquid with particulate silica particles which have been coated with a surface active agent to render the silica particle hydrophobic. One problem inherent in the use of this method arises from the fact that not all of the pollutant liquid is consumed and the residue agglomerates with the silica particles leaving crusty patches of siliceous pollutant residue floating on the water's surface. The pollutant residue must be scooped or otherwise removed from the surface.

SUMMARY OF THE INVENTION

In accordance with the process herein described, a plurality of cellular ceramic nodules are deposited on the free surface of the combustible liquid to be burned so that they float thereon. The nodules are wetted by the combustible liquid and then the liquid is ignited and burned on the exposed upper surface of the nodules remote from the major portion of the layer of liquid being burned. Combustion of the liquid on the exposed upper surface of the nodule is thereafter continued in a substantially self-sustaining manner until substantially all of the combustible liquid has been burned or consumed in the combustion process.

The process includes isolating a portion of the combustible liquid as a film on the upper surface of the nodules so that the film of combustible liquid is separated from the body of water. On the upper exposed surface of the nodule, remote from the body of water, ignition and sustained combustion of the liquid takes place. The film of combustible liquid on the upper surface of the nodule is continually replaced with liquid from the layer of combustible liquid through capillary action.

Accordingly, it is an object of this invention to provide a process for substantially completely burning a liquid pollutant and thereby removing the liquid pollutant from the surface of a body of water.

Another object of this invention is to provide a process for enabling or enhancing the combustion of a combustible liquid which is otherwise difficult to ignite or difficult to sustain combustion.

DESCRIPTION OF THE PREFERRED EMBODIMENT

This invention provides an improved process for removing liquid combustible pollutants from a body of water and for enabling and enhancing the combustion of liquids generally. The cellular ceramic nodules deposited on the upper free surface of the combustible liquid enable and enchance the combustion that results in the complete combustion and removal of the combustible liquid from the surface of the body of water. Although it is not completely understood how the cellular ceramic nodules enhance and maintain the combustion of the liquid, it is believed the nodules isolate portions of the combustible liquid from the layer in contact with the body of water and continually replace the isolated liquid burned by other liquid from the layer floating on the body of water until substantially all of the liquid is thereby burned. It should be understood, however, that there is no intention to be bound by the above or any of the following explanations concerning the manner or mechanisms through which this invention functions.

The cellular ceramic nodules suitable for use in this process may be prepared in accordance with the process described in U.S. Pat. No. 3,354,024 from a pulverulent glassy material and a cellulating agent or from other pulverulent materials and a cellulating agent in accordance with the process described in U.S. Pat. No. 3,441,396. A description of the process for providing a textured surface on the nodule may be found in copending application Ser. No. 727,242, filed May 7, 1968, now U.S. Pat. No. 3,493,218, and entitled "Tower Packing Element". The cellular ceramic nodules enable and enhance combustion of the combustible liquid to be removed from the body of water through interaction of the physical characteristics of the nodules, such as the surface morphology, the density the impermeability, the chemical composition, the thermal characteristics, and the like. The nodules may have an apparent density of between about 6 and 30 pounds per cubic foot and a thermal conductivity of between about 0.40 to 0.50 Btu./hr./sq.ft./°F./in. at 75° F. The nodules can be made in many different sizes. Nodules of a size between one-eighth and one-half inch with an apparent density of between 10 and 20 pounds per cubic foot were found suitable.

In U.S. Pat. No. 3,354,024 the nodules are made by admixing relatively fine pulverulent glass with a cellulating agent such as carbon black or the like. A binder is then added to the mixture which is then pelletized and subsequently coated with a parting agent that serves to maintain the pellets discrete during the cellulation process. The coated pellets are heated in a rotary furnace or kiln to a cellulating temperature and the pellets cellulate to form substantially spherical cellular ceramic nodules with a continuous outer skin. Although pulverulent glass is a preferred constituent of the cellular ceramic nodules, other glassy materials as described in U.S. Pat. No. 3,441,396 may be used. The term ceramic is intended to encompass both pulverulent formulated glass and other suitable pulverulent glassy materials.

The cellular ceramic nodules thus produced have a core of individual completely closed cells of ceramic material and a continuous outer skin of ceramic material. For use with the herein described process, it is preferred that the cellular ceramic nodules produced as described above be abraded or otherwise treated to remove the relatively thin continuous outer skin and a portion of the layer of underlying closed cells to expose, over the entire surface of the nodule, a portion of the layer of cells therebeneath. The cells on the abraded surface are opened to form a surface having a plurality of contiguous individual cup like recessed portions or cell fragments. Since the outer surface of the abraded nodules appears as an irregular textured surface, for brevity the plurality of concave cup shaped depressions comprising the outer surface of the abraded nodules will be referred to hereinafter as an irregular textured surface.

The cellular ceramic nodules produced as described above exhibit many characteristics which are readily and preferentially adaptable for the herein described process. For example, in this process the combustion enhancing agent should be impervious or impermeable to the flow of fluids into and through the combustion enhancing agent. Therefore, all of the liquid to be burned remains on the surface of the combustion enhancing agent and is accessible for combustion and ultimate burning. The combustion enhancing agent remaining after combustion of the combustible liquid is substantially devoid of the combustible liquid, thereby obviating further treatment or purification of the combustion enhancing agent.

The nodules have a density less than the density of the water and preferably less than the density of the liquid to be burned. It is essential that the nodules float on the upper surface of the water and preferably on the upper free surface of the liquid to be burned. It is also preferred that the nodules float on the liquid to be burned with only a portion of the nodule submerged below the surface of the liquid to be burned. Nodules produced as previously described generally have an apparent density of between about 6 pounds per cubic foot and 30 pounds per cubic foot. Nodules with a density of the above range have exhibited a high degree of efficiency when used in this process.

Another preferred property of the combustion enhancing agent is that the agent have a chemical composition that is inert and unreactive with the material to be burned as well as with the surrounding atmosphere and the body of water on which it floats. The cellular ceramic nodule is chemically inert with respect to combustible liquid hydrocarbons, air and water so that the surface morphology of the nodule will not be altered substantially during the combustion process and the density and other desirable properties of the nodule will not be altered substantially during the combustion of the combustible liquid thereon.

Although it is preferred that the outer surface of the cellular ceramic nodule be irregular and textured with a continuum of contiguous concave cell portions, it is preferred that the gross configuration of the nodule be substantially spherical. The substantially spherical configuration provides greater efficiency and is therefore preferred. However, the process can be practiced even with an inventory of nodules that exhibit a substantial degree of nonsphericity.

The size of the cellular ceramic nodule is a function of several parameters, among which are the nature of the liquid to be burned; the specific composition and unique morphology of the cellular ceramic nodule employed; the cell size of the nodule; the ambient physical conditions around the system comprising the nodule; the combustible liquid to be burned, and the underlying water; and the temperature and other physical and chemical characteristics internal to the system comprising the nodules and the two liquids. In some relatively common circumstances nodules having a diameter of between about one-eighth inch and one-half inch were found suitable for use in this process. In use with common crude oil and other petroleum products, nodules having a diameter of about one-fourth inch were found to be highly effective for use in this process.

It is believed that the thermal properties of the cellular ceramic nodules contribute substantially to the combustion process. The efficiency of combustion and of liquid removal are substantially enhanced where the combustion enhancing agent operates in the physical system as a thermal insulator between the body of water and the film of combustible liquid on the surface of the nodule. The nodules used in this process have a thermal conductivity substantially lower than the combustible liquid. With crude petroleum, other common petroleum products and other hydrocarbon liquids, nodules having a thermal conductivity of between about 0.40 and 0.50 Btu./hr./sq. ft./° F./in. at 75° F. function extremely efficiently and result in the complete combustion and removal of the combustible liquid with no residue remaining in the system.

To maintain a continued burning efficiency, it is also desirable that the melting point of the nodules be substantially higher than the flash point and combustion temperature of the combustible liquid. The cellular ceramic nodules produced according to the above described process maintain their physical integrity and surface morphology up to temperatures of about 1,600° F. The use of nodules having a high melting point is also desirable because the process has been found to enhance both the temperature and the rate of combustion for a given combustible liquid. The high melting point enables and supports extremely rapid and complete combustion of the combustible liquid and reduces the amount of unburned hydrocarbons introduced into the atmosphere.

It appears, as the nodules float in the liquid to be burned, that the liquid is lifted from the layer in two ways. First, the liquid forms a thin film around the exposed outer surface of each cellular ceramic nodule and that film is maintained in place by the attractive or adhesive forces generated by the intermolecular forces and attractions between the molecules of the liquid and the cellular glass nodules. Secondly, it is believed that surface capillarity on the surface of the nodule takes place in that preferentially the film of combustible liquid rises onto the exposed nodule surface from the surrounding layer of combustible liquid and the film is continually replaced from the layer by this surface capillarity.

Because of the formation of the thin film of liquid around each nodule and the continued replacement of the liquid, the process functions efficiently if only a monolayer, or partial monolayer, of cellular ceramic nodules are positioned on the surface of the combustible liquid.

The ignition and combustion of the combustible liquid is sustained in a combustion zone which may be defined as the upper or exposed surface of the cellular ceramic nodules remote from the underlying body of water. In most instances, the creation of the thin film of liquid permits ignition of the liquid by the mere application of heat by means of an open flame on the upper surface of the nodules. In some circumstances, however, where the combustible liquid is not readily ignitable, an igniter such as a highly flammable fluid which has a relatively low flash point can be added to the combustible liquid to facilitate ignition of the combustible liquid. It should be noted, however, that only a relatively small amount of the igniter need be added to the combustible liquid to initiate ignition. After ignition is initiated there is a flame spread across the other nodules in the layer to propagate combustion throughout the entire layer of nodules.

During combustion the amount of liquid supplied to the combustion zone, that is the upper surface of the cellular ceramic nodules, is, in this process, optimized in the sense that sufficient liquid is supplied to the combustion zone to support rapid, high temperature combustion while excess combustible liquid is maintained below or out of the combustion zone, thereby preventing the wasteful transfer of heat through the combustible liquid to portions of that liquid not being burned in the combustion zone. In addition, the zone of combustion is maintained at the upper surface of the cellular ceramic nodules which have the previously discussed thermal insulating properties, thereby separating the heat source from the underlying water and minimizing the heat loss to the body of water therebelow.

With their low thermal conductivity, the nodules function as thermal insulators during combustion thereby preventing loss of heat to the underlying water and confining and concentrating the available heat to the region of combustion in the thin film of liquid on the surface of the nodules.

The creation and maintenance of a restricted and insulated combustion zone with a continuous supply of combustible material provides a highly efficient thermal system effecting complete combustion of the liquid at unusually high temperatures and rapid combustion rates. The observed combustion obtained with this process leaves substantially no residue on the surface of the water other than the nodules and provides less noxious fumes and smoke.

The impervious nature of the cellular ceramic nodules prevents the absorption of liquid into the nodules themselves with the result that all of the liquid is maintained available for combustion and the surface area of the nodules remains unchanged throughout the process to provide a relatively fixed combustion zone.

A substantially spherical shape of the nodules is preferred in their use in this process because the spherical characteristic provides only point contact between contiguous nodules so as not to interfere substantially with capillary spaces between the nodules. It is also believed that the surface morphology of a spherical nodule contributes substantially to the film formation of the combustible liquid previously discussed.

In certain circumstances, such as on a large body of water, it is not always possible to completely cover the surface of the combustible liquid with a layer of cellular ceramic nodules. It appears, however, during the combustion process, that the combustible liquid is drawn into the area of the nodules and upwardly into the combustion zone by the kinetic effects of combustion and the intermolecular cohesion between the liquid molecules and adhesion between the liquid molecules and the cellular ceramic nodule. Where necessary, the process can be performed over successive areas of the body of water by confining the combustion process within a suitable boundary element such as a floating ceramic or insulated metal container or fence. The following examples are merely illustrative and are not intended to limit this invention.

EXAMPLES

The process was practiced in a cylindrical container having a height of about 20 inches and a diameter of about 10 feet and filled with water to a location within about 6 inches of the brim. Motion was imparted to the water by wave machine to form waves having a 4 to 5 inch height. As a comparison, a test was performed in which the water was covered with a relatively thin film of Ohio crude oil which was readily ignited without the presence of cellular ceramic nodules but which was incapable of sustaining combustion without the addition of a combustion enhancing agent. Without the cellular ceramic nodules a large amount of unburned residue remained after combustion terminated and it appeared that only the low boiling constituents of the Ohio crude oil were consumed. In a subsequent test, cellular ceramic nodules having a diameter of about one-fourth inch and an apparent density of 17 pounds per cubic foot were floated on the upper surface of the layer of Ohio crude oil. It appeared that a film of the crude oil formed on the upper surface of the nodules. The film on the upper surface of the nodules was ignited by an open flame from a propane torch and could be considered as almost instantaneous. Combustion of the crude oil with the nodules floating on the upper surface thereof was extremely rapid and self-sustaining. After the combustion had terminated, the nodules were examined and the nodule surfaces were dry and substantially devoid of oil. The surface of the body of water was clean with little or no residue remaining. The temperature of the water adjacent the upper surface thereof appeared to be substantially the same as the temperature of the water a substantial distance therebelow, indicating that little, if any, of the heat of combustion was transferred through the nodules to the body of water therebelow.

Another series of tests were conducted using a commercially available grade of motor oil rated at SAE 30, HD–1 certified 101–B and 6041–M. The motor oil had a flash point of 430° F. and a fire point 480° F. From the combustion it did not appear that the motor oil contained any highly volatile hydrocarbon fractions. A layer of the motor oil was poured onto the upper surface of a body of water. Without the nodules, the oil could not be ignited with a propane torch. The addition of a low flash point igniting agent did not sustain combustion of the motor oil without the nodule combustion enhancing agent.

A layer of cellular ceramic nodules having a diameter of about one-fourth inch and an apparent density of about 17 pounds per cubic foot were floated on the upper surface of the motor oil. A few millimeters of a low flash point igniting agent were added to the motor oil at one location on the surface. The motor oil in the vicinity of the igniting agent was easily ignited by an open flame from a propane torch. After ignition, combustion was continuous and spread over the entire surface of the container. It appeared that combustion was taking place on the upper surface of the cellular ceramic nodules. The combustion of the motor oil was rapid and complete. The surface of the water after combustion terminated appeared clean with little or no residue remaining and the cellular ceramic nodules were dry and substantially devoid of residue.

A third series of tests under equivalent conditions were conducted with Ohio crude oil using ¼ inch cubes of foamed polyurethane instead of cellular ceramic nodules. In those tests, combustion was not self-sustaining and a substantial amount of heavy oil residue remained. In addition, the urethane absorbed a substantial volume of oil, forming a sticky mass which exuded large amounts of oil when squeezed or compressed.

A similar series of tests were performed using polystyrene beads as a combustion enhancing agent. The polystyrene beads produced very poor combustion with rapid degredation of the polystyrene leaving a charred layer of carbonaceous material and a heavy unburned oil residue.

As will be apparent from the above description, the process of this invention provides a means for ignition and complete combustion of a liquid with complete combustion of even the heavy and less combustible constituents of that liquid. Combustion occurs rapidly and at high temperatures, reducing the volume and noxious nature of the smoke and fumes produced thereby avoiding or reducing pollution of the atmosphere. The water on which the layer of combustible liquid was floating is left clean and uncontaminated and the nodules remaining present no problem and do not require removal from the area. The nodules as previously discussed are substantially free of the oil residue and if left on the surface of the water are not harmful to human beings or to plants or animals. Eventually, the nodules will abrade against each other and disintegrate, or if washed up on a beach or stream bank, will eventually disintegrate by abrasion due to wave action and be assimilated into the soil of the area. The nodules, although made of a glassy or ceramic material, do not have sharp edges in the sense that they do not cut the surface of the skin and are therefore harmless to persons coming in contact with the cellular ceramic nodules.

According to the provisions of the patent statutes, we have explained the principle, preferred construction and mode of operation of our invention and have illustrated and described what we now consider to represent its best embodiment.

We claim:

1. A process for burning a combustible liquid comprising, floating impermeable discrete particulate material on the surface of a body of combustible liquid with a portion of said particulate material above the surface of said body of combustible liquid and a portion below the surface of said body of combustible liquid, forming a relatively thin film of said combustible liquid on the upper exposed surface of said discrete particulate material, said particulate material having insulating properties to insulate said thin film of combustible liquid from said body of combustible liquid, igniting and burning said combustible liquid in said thin film, and continuously replacing the burned combustible liquid in said thin film with combustible liquid from said body of combustible liquid by separating a film of said combustible liquid from said body of combustible liquid and positioning said film on the upper exposed surface of said particulate material.

2. A process for burning a combustible liquid as set forth in claim 1 in which, said body of combustible liquid comprises a layer of combustible liquid floating on the upper surface of a body of water, and insulating said thin film of combustible liquid from said body of water.

3. A process for burning a combustible liquid as set forth in claim 2 in which said layer of combustible liquid is crude oil.

4. A process for burning a combustible liquid as set forth in claim 2 in which said combustible liquid is not readily ignitable with an open flame, adding A small quantity of a readily ignitable combustible liquid to said layer of combustible liquid at a preselected location, and igniting that portion of said combustible liquid containing said readily ignitable combustible liquid.

5. A process for burning a combustible liquid comprising, floating a plurality of impermeable cellular ceramic nodules on the upper surface of a body of combustible liquid with the upper portion of said cellular ceramic nodules exposed above the upper surface of said body of combustible liquid and a portion of said cellular ceramic nodules below the surface of said body of combustible liquid, forming a relatively thin film of said combustible liquid on the upper exposed surface of said nodules, igniting and burning said combustible liquid in said thin film, and continuously replacing said combustible liquid in said thin film from said body of combustible liquid.

6. A process for burning a combustible liquid as set forth in claim 3 which includes, wetting the exposed upper surface of said nodules with said combustible liquid.

7. A process for burning a combustible liquid as set forth in claim 5 in which said cellular ceramic nodules are substantially spherical in shape.

8. A process for burning a combustible liquid as set forth in claim 5 in which, said cellular ceramic nodules have a textured irregular outer surface.

9. A process for burning a combustible liquid as set forth in claim 5 which includes, depositing a monolayer of cellular ceramic nodules on the upper surface of said body of combustible liquid in a manner that said adjacent nodules are in contiguous relation to each other.

10. A process for burning a combustible liquid comprising, floating a plurality of impermeable cellular ceramic nodules on the surface of a body of liquid comprising a layer of combustible liquid floating on the upper surface of a body of water, said cellular ceramic nodules having an upper portion exposed above the surface of said layer and a portion below the surface of said layer, forming relatively thin films of said combustible liquid in said layer on the upper exposed surfaces of said cellular ceramic nodules, insulating said thin films of said combustible liquid from said body of liquid by said cellular ceramic nodules positioned between said thin films and said body of liquid, igniting and burning said combustible liquid in said thin film, and continuously replacing said combustible liquid in said thin film from said body of combustible liquid.

11. A process for burning a combustible liquid as set forth in claim 10 in which, said cellular ceramic nodules are substantially spherical in shape and have a diameter greater than one-eighth inch, wetting the exposed upper surface of said cellular ceramic nodules with said combustible liquid, continuously replacing said thin film of combustible liquid by separating a film of said combustible liquid from said layer and having said film flow along the upper exposed surface of said cellular ceramic nodules.

12. A process for burning a combustible liquid as set forth in claim 10 in which, said cellular ceramic nodules are substantially spherical in shape and have a textured irregular outer surface, said cellular ceramic nodules having a density less than 30 lb./cu. ft. and a diameter of between about one-eighth and one-half inch.

13. A process for burning a combustible liquid as set forth in claim 10 in which, said cellular ceramic nodules are substantially spherical in shape and have a textured irregular outer surface, depositing a monolayer of said cellular ceramic nodules on the upper surface of said layer of said combustible liquid in a manner that said adjacent cellular ceramic nodules are in contiguous relation to each other.

14. A process for burning a combustible liquid as set forth in claim 13 in which said combustible liquid is not readily ignitable with an open flame, adding a small quantity of a readily ignitable combustible liquid to said layer of combustible liquid at a preselected location, and igniting that portion of said combustible liquid containing said readily ignitable combustible liquid.

* * * * *