# United States Patent

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[72] Inventors **Stefan Kraemer**
**Essen;**
**Alois Seidl, Thurnstein; Michael Seger,**
**Krefeld-Linn, all of, Germany**
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[73] Assignee **WASAG Chemie Akliengesellschaft**
**Essen, Germany**
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## [54] PROCESS OF BURNING AWAY OIL OR OTHER COMBUSTIBLE LIQUIDS ON WATER OR OTHER NON-COMBUSTIBLE LIQUIDS

**9 Claims, No Drawings**

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[56] **References Cited**

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*Primary Examiner*—Samih N. Zaharna
*Attorney*—Krafft & Wells

**ABSTRACT:** A process for absorbing and burning away oil or other combustible liquids on water or other noncombustible liquids wherein absorbent and/or surface active noncombustible inorganic foamed particles are spread out over the combustible liquid, the combustible liquids are absorbed by the particles and the liquid absorbed by the particles is ignited.

# PROCESS OF BURNING AWAY OIL OR OTHER COMBUSTIBLE LIQUIDS ON WATER OR OTHER NON-COMBUSTIBLE LIQUIDS

## CROSS-REFERENCES TO RELATED APPLICATIONS

Applicants claim priority under 35 U.S.C. 119 for application Ser. No. 17 08 522.2, filed in the Patent Office of the Federal Republic of Germany on Mar. 6, 1968.

The disclosure of copending Application Ser. No. 778,800, of Alois Seidl and Stefan Kraemer, filed in the U.S. Pat. Office on Nov. 25, 1968, now abandoned is incorporated herein. Application Ser. No. 778,800 is a continuation-in-part of application Ser. No. 534,431, filed Mar. 15, 1966, and is entitled "Ceramic Granular Fillers, Process of Producing the Same and Articles Molded Therefrom," now abandoned.

## BACKGROUND OF THE INVENTION

The field of the invention is a process for absorbing and burning away of oil or other combustible liquids on water or other noncombustible liquids.

By the term "other noncombustible liquids" applicants intend to include besides fresh water, aqueous solutions such as sea water.

By the term "combustible liquids" applicants intend to include volatile motor fuels and Diesel fuels, such as kerosene, crude oil and its fractions, fuel oils of the various kinds from the lighter grades to extremely heavy kinds, such as Bunker-C oil, Massut, etc., in short all liquids which float upon water which are regularly transported or are exploited from the ocean or inland waters.

It is known that oil which is floating upon water can be absorbed by foamed synthetic materials. Besides the large quantities of absorbing material that would be required, for example after a tanker accident, the transportation of which to the scene of the accident would be quite a problem, there would also remain the problem of disposing of the oil that has been absorbed. There is usually no alternative expect to let the absorbed oil gradually accumulate along the coasts, whereby the usual damage will be done. Such a method of disposal is, therefore, inadequate and undesirable.

The apparently obvious method of disposal of the oil by igniting it and burning it away on the water is not possible without the use of absorption materials if the oil layers are up to several decimeters thick. As soon as the burning layer of oil drops below a minumum thickness as determined by the flash point, the flame is extinguished at the instant when the heat transmission away from the oil through the water layer cools the oil to a temperature below the flash point. Even with the use of foamed synthetic resin particles for absorbing the oil, a continued burning away of the oil is not possible. Although with the strong capillary action and heat insulating ability of the synthetic resin it is not difficult to ignite the oil, still the flame is extinguished in a short time.

The reasons therefor are many, but are postulated as follows—many organic substances are oil-soluble, especially in oils containing aromatic and naphthenic components which will nullify their absorbing and heat insulating ability. After the ignition the temperature at the boundary surface between the absorption material and the oil flame rises so rapidly that the melting point of the synthetic resin is reached and the process is thereby interrupted.

The state of the prior art raw materials for the present invention may be ascertained by reference to U.S. Pats. No. 3,184,371, patented May 18, 1965, and 3,261,894, patented July 19, 1966, of Alois Seidl; the Kirk-Othmer "Encyclopedia of Chemical Technology," 2nd Ed., Vol. 10 (1966) under the section "Glass," pages 533—604, particular pages 538 to 546 dealing with compositions, and 550—561 dealing with raw materials; and the Modern Plastics Encyclopedia (1966) under the section "Silicones," pages 313—324, particularly page 324 where water repellency is disclosed.

According to U.S. Pats. No. 3,184,371 and 3,261,894, silicate particles are produced by dissolving 0.02—0.7 parts of an inorganic fibrous silicate in 1 part alkali metal silicate and 2—10 parts of water. The mixture is heated to about 140°—300° C. to drive off any free water phase and the substantially dried mass is comminuted to obtain particles of 0.1 to 10 mm. The densities of the final products are decreased by employing inorganic or organic blowing agents. When inorganic sulfates, such as zinc sulfate or aluminum sulfate, are admixed with the preliminary product in a ratio of 0.05 parts by weight blowing agent to 100 parts by weight of preliminary product, it is possible to obtain densities of about 0.20 to 0.15 grams per cu. centimeter.

Of the enumerable possible water-soluble organic blowing agents that are employed, particular success was achieved with sugar, molasses, glycerin and ethylene glycol. These water-soluble substances are preferably admixed to the alkali silicate solutions in such concentrations by weight that the carbon introduced amounts to about 0.01 to 2 percent, even more preferably 0.05 to 0.5 percent. The final products made with organic blowing agents have densities in the order of 0.05 to 0.15 grams per cu. centimeter.

According to the disclosure of Application Ser. No. 778,800, granular fillers are produced by:

1. dissolving a fibrous inorganic silicate in aqueous alkali metal silicate solution in the proportion of 0.02 to 0.7 parts by weight of fibrous inorganic silicate to 1 part of the aqueous alkali metal silicate;
2. drying the solution;
3. granulating the product;
4. coating the granules with substances having high melting points such as lime; and
5. heating the coated product between about 600°—1,000° C.

In the fourth step of Application Ser. No. 778,800, the granular material is wetted with an aqueous suspension of inorganic compounds, such as lime, chalk, zinc oxide, alumina, iron oxide or the like. The high melting inorganic compounds have a melting point of between about 1,200° and 2,500° C. About 25—100 parts by weight of granulated material are coated by 1 part by weight high melting inorganic compound, where the inorganic compound is dispersed in water.

In another particular embodiment of the disclosure of Application Ser. No. 778,800, the granular end product is treated with a metal soap or a silicon oil. The treated granular product is useful in selectively absorbing oil or water dispersions.

## SUMMARY OF THE INVENTION

The purpose of this invention is to provide a process by which great damage to the domestic economy and biology by oil contamination is avoided. According to the present invention, absorbent and/or surface active incombustible and possibly hydrophobic foamed particles of inorganic materials, metal oxides, etc. or combinations thereof, are applied upon the combustible liquids floating on the water or other noncombustible liquid. The combustible liquids include those substances which at room temperature are pasty or solid, but which liquefy at temperatures above 20° C. The foamed particles have a lower specific gravity than the liquid to be burned, and are able to absorb the liquid. The absorbing ability is between 10 and 500 percent of the weight of the foamed particles.

It is not absolutely necessary for the foamed particles to be rendered hydrophobic, and especially not if they are spread over a thick layer of the combustible liquid. With thin layers whose thickness is less than 1–2 mm., it is, however, necessary for the foamed particles to absorb the oil selectively from the water surface to permit complete combustion of the oil.

The particles are rendered hydrophobic by the usual methods. Especially effective for this purpose are the silicones which are applied by atomization or vaporization. The foamed particles preferably range in size from 1 to 30 mm. The granules can be of approximately uniform size, or can be a mixture of different sizes. Particles of large surface area, such as foamed glass plates, are also useful.

The surface active noncombustible inorganic foamed particles of the present invention include broken fragments of inorganic foamed material having a maximum size which does not exceed 5 cm. The particles may also be plates of inorganic foamed material, such as the waste plates produces by the foamed glass manufacturing method of U.S. Pat. No. 3,261,894, and these plates may be up to 5 cm. thick and up to 0.5 sq. meters in size.

Globular or cylindrical particles useful in the present invention are produced according to the disclosure of Application Ser. No. 778,800.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Suitable substances of which the foamed glass particles are produced are siliceous substances such as sodium, calcium or aluminum silicate, alone or in mixtures, expanded mica or similar expanded natural products, but also oxidic materials such as $A1_2O_3$ and clay, and even foamed metals, especially aluminum and its alloys when they function as absorbers and remain floating on the surface of the liquid, which means that in addition to the open pores which give the material wicklike properties, it also has enough closed air cells to keep it floating.

The foamed materials which are especially suitable for absorbing and burning oil that is floating on a water surface are disclosed in U.S. Pats. Nos. 3,184,371 and 3,261,894, and Application Ser. No. 778,800. During the production of these materials the ratio of the opening pores to the closed inner cells is controlled within wide limits by the use of varying amounts of foaming agent. These foaming agents include calcium carbonate, aluminum sulfate, zinc sulfate, carbon compounds such as glycerol, sugar and others in the presence of sulfates, and also compounds containing chemically bound water. The melting point of the products thus produced are varied within wide limits, at least between 400°—1,000° C.

The melting point of the foamed glass particles is brought up to at least 400° C. by addition of lead, boron etc. compounds to the aqueous silicate solution. Lead compounds suitable for this purpose are preferably lead oxides PbO, $PbO_2$ and $Pb_3O_4$, while suitable boron compounds are, for example borax and other borates. The melting points of the foamed glass are brought to a maximum of 1,000° to 1,100° C. by the addition of alkaline earths and earth metals to the foamable silicate solution. Reference is here made to compounds of the alkaline earths and of the elements of main group III of the periodic table, such as aluminum, etc., and especially in the oxide form.

By suitable adjustment of the porosities and melting points it is possible to produce products that are suitable for absorbing and burning away of oils, etc., and which after completion of the burning away process become sintered at their surfaces and in the manner acquire sufficient density to sink in the water. In a similar manner other products are obtained which will retain their closed air cells in sufficient abundance to keep them floating on the surface after the burning has ended.

The products of combustion are preferably allowed to escape into the air while some of the ash remains in the foam. After the burning, the foam remains floating on the surface if it retains sufficient porosity to keep the densities of the floating particles less than the densities of the liquids. This is accomplished by using glasses, metal oxides or expansible clay of high melting point for the production of foamed particles. The foamed material will, however, sink if the closed pores are lost sufficiently to give the foamed material a greater density than the noncombustible liquid. This result is produced by the use of low melting glasses as starting materials.

It is preferred that the foamed particles remain floating after the combustion because they can then be brought on land and collected without soiling the coast or acting unfavorably upon

the marine fauna. If, however, economic considerations are controlling, then those foamed particles should be preferred which will sink after the burning, because the original raw materials are very cheap.

The treatment of the foamed particles to render them hydrophobic is accomplished in many ways with industrial silicone oils (produced from organosiloxanes derived from alkylhalogen silanes) which are dissolved in organic solvents, the foamed particles being sprayed with the silicone solution or immersed therein. The silicone oils are also applied as aqueous emulsions, or in the form of their precursors (e.g. mono-, di- and tri-chlor-silanes) which by hydrolysis with steam are coated upon the foamed particles. The water-repelling agents are also vaporized upon the foamed particles under vacuum. From this it is seen that silicone oils or their precursors are applied in many ways. The foamed particles are also rendered water-repellent by other known methods, e.g. by coating them with oils such as heating oil, asphalt, mineral fats, waxes such as montan wax or ozocerite, but also with salts of fatty acids, e.g. calcium stearate in solution, suspension, emulsion or dispersion.

The substances used in the present invention have the following characteristics—they are inorganic silicious, oxidic or metallic foam, the last three of which can be used either separately or in mixtures of two or three. They are incombustible, buoyant, insoluble or only slightly soluble in water, insoluble in oil, absorbent for liquids that do not dissolve in water, stable in the presence of water and only slightly swellable or not swellable at all. Their affinity for combustible liquids is greater than their affinity for water.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extend. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the specification and claims in any way whatsoever.

### EXAMPLE 1.

A preliminary solution was prepared from 1 liter of alkali silicate solution ( 32 percent potassium silicate solution) and 3 g. crystallized sucrose dissolved in 40 cm.$^3$ of water. 150 g. rock wool and 1 liter of this aqueous preliminary solution were thereafter mixed with 0.7 liter of water. The rock wool was completely dissolved by heating, and the solution was then evaporated in an iron vessel for 6 hours at 300° C. The solid residue was removed after cooling, and crushed in a conventional grinder to a maximum grain size of 10 mm.

### EXAMPLE 2.

One liter of waterglass ($Na_2SiO_3$) is diluted with 500 cc. water containing in solution 3 g. $ZnSO_4$ and 4 g. glycerol. 50 g. rock wool are then added and the mixture is evaporated down with constant stirring until the rock wool is dissolved and the total mixture still contains 55—65 percent water. After being further dried to a water content of 5—20 percent, the hard product is comminuted and screened to a granular diameter of 0.5—2 mm. The granular preliminary product thus obtained is immersed in a lime suspension and then heated in a mold to a melting temperature between 600 and 900° C. After fusion of the material the mold is removed from the oven and emptied. Globules of foamed glass of 2 to 10 mm. diameter are formed in the mold without being merged into one another. These very light globules have an apparent specific gravity of 80 g./1.

### EXAMPLE 3.

A concrete trough is filled with water. Upon the water surface of 4 m.$^2$, 4 liters of light heating oil are poured which spreads out evenly on the water in a layer about 1 mm. thick. At one place 2 liters of porous, absorbent water repellent foamed glass spherical particles produced according to example 2, of 2—10 mm. diameter and an apparent density of 80 g./liter are deposited on the oil covered water. The particles absorb 300 percent of their weight of oil. They were rendered water repellent with dichlor-silane by vapor coating in vacuum. The oil coated foamed glass particles are then ignited with a match. The flame immediately spreads out over the entire surface of the trough that is covered by these foamed glass particles while the remainder of the surface that was covered by oil alone did not ignite. Although only a portion of the surface of the trough took fire, practically the entire surface was cleared of oil, leaving only interference colors as a reminder of the oil. Most of the foamed glass particles eventually spread out over the surface of the water, with only a few of them sinking to the bottom.

## EXAMPLE 4.

The same experiment as above is repeated with heavy heating oil upon salt containing water. Since the oil is viscous, 4 liters of spherical particles of absorbent expanded clay (which were produced by rapid heating of granulated clay and which were rendered water repellent by spraying with liquid bitumen), are spread uniformly over the surface of the oil covered water. The material is ignited by a bushel of burning excelsior thrown upon the oil-covered water surface. The burning spread out in all directions from this place until every trace of oil has been burned up, and after the burning is completed the spherical particles of expanded clay remain on the surface of the water without sinking.

## EXAMPLE 5

In the same experimental trough as examples 3 and 4, absorbent pieces of foamed glass produced by example 1 and rendered water repellent by an alcoholic solution of calcium stearate are distributed in a layer about 4 cm. thick on half of the liquid layer consisting of water covered by a layer of oil 4 mm. thick. After being ignited by a small fuse, the oil surface burns completely away. During the burning many of the particles of foamed glass disintegrated into smaller pieces. Most of the foamed glass particles are sintered together sufficiently during the burning process to cause them to sink.

We claim:

1. A method for absorbing and burning away combustible liquids floating upon water comprising spreading over said combustible liquids inorganic foamed particles having a melting point between 400°—1,100° C. and a density of 0.05 to 0.20 grams per cubic centimeter which are incombustible, buoyant, substantially insoluble in water, insoluble in oil and having an absorption affinity for said combustible liquids greater than the affinity for water to absorb said combustible liquids, and igniting said absorbed combustible liquids.

2. The method of claim 1, wherein said foamed particles absorb from about 10 to 500 percent of their weight of the combustible liquid.

3. The method of claim 1, wherein said foamed particles are floatable and remain so after said combustible liquids are burned away.

4. The method of claim 1, wherein said foamed particles are floatable and lose their floatability and sink after said combustible liquids are burned away.

5. A method for absorbing and burning away combustible liquids floating upon water comprising:

a. dissolving about 0.02—0.7 parts by weight of an inorganic fibrous silicate in about one part by weight aqueous alkali metal silicate containing a blowing agent;

b. heating the dissolved mixture to about 140°—300° C. to a substantially dry mass;

c. comminuting the mass and heating the comminuted mass to about 700°—900° C. to produce inorganic foamed particles having a melting point between 400°—1,000° C. and a density of 0.05 to 0.20 grams per cubic centimeter;

d. spreading said inorganic foamed particles over said combustible liquids floating upon water to absorb said combustible liquids; and

e. igniting said absorbed combustible liquids.

6. The method of claim 5, further comprising applying a hydrophobic coating to said inorganic foamed particles.

7. The method of claim 5, wherein the comminuted mass comprises fragments less than about 5 cm. in diameter.

8. The method of claim 5, wherein the comminuted mass is molded into plates having a size configuration less than about 5 cm. thick and 0.5 square meters.

9. A method for absorbing and burning away combustible liquids floating upon water comprising:

a. dissolving about 0.02—0.7 parts by weight of an inorganic fibrous silicate in about one part by weight aqueous alkali metal silicate containing a blowing agent;

b. heating the dissolved mixture to about 140°—300° C. to a substantially dry mass;

c. comminuting the mass and coating the comminuted mass with a dispersion of a high melting inorganic compound having a melting point between about 1,200°—2,500° C.;

d. heating the coated comminuted mass to about 600°—1,000° C. to produce inorganic foamed particles having a globular or cylindrical shape;

e. spreading said inorganic foamed particles over said combustible liquids floating upon water to absorb said combustible liquids; and

f. igniting said absorbed combustible liquids.