United States Patent Office

2,816,863

Patented Dec. 17, 1957

2,816,863

COMBUSTIBLE GAS SENSING ELEMENTS

Carl M. Page, Van Nuys, Calif.

No Drawing. Application February 2, 1954, Serial No. 407,815

7 Claims. (Cl. 252—1)

The present invention relates to combustible gas sensing agents in general and particularly to such agents sensitive to mixtures of combustible gases with air or oxygen. More specifically the invention relates to a combustible gas sensing agent, and to a method for its preparation and application, of the type adapted to sense the presence of combustible gas mixtures within certain ranges and to support combustion without flame upon its surface and within its body in the presence of such gas mixtures.

The present application is a continuation-in-part of earlier filed application Serial No. 325,707, filed December 12, 1952, now abandoned.

Many highly volatile liquids give off combustible gases which are explosive in the presence of air or oxygen within certain mixture ranges. Mixtures which are too lean or too rich, that is, below or above the range of explosibility for that particular gas, are non-explosive. It is frequently desirable in commercial applications of combustible gas detecting instruments to determine the presence or absence of combustible gas mixtures within certain predetermined ranges. A specific example is the determination of the percentage mixture composition of a dangerous mixture of combustible gas and air or oxygen within the range supporting explosion. It is, in fact, also extremely desirable to be able to determine the percentage mixture composition of any combustible mixture, either below or above the explosive range.

There are certain sensing agents, comprising metals of the so-called "platinum group" or "heavy metal group," which effect combustion without flame upon their own surfaces and within their pores in the presence of a mixture of many combustible gases and air or oxygen, both within above and below the combustible range. Such gases may be divided broadly into gases readily catalyzed into combustion, and more resistant gases. As to the ordinary gases, such as ether, alcohol, acetone, and petroleum vapors, a "heavy metal" sensing agent will function to effect combustion within the explosive range of such mixtures, and even below the "lower explosive limit" of the mixture down to a point where only a trace of the combustible gas is present. The word "trace" is used here and elsewhere in its dictionary meaning, i. e. a barely detectable quantity, not quantitatively determined because of minuteness. This availability of ordinary sensing agents is desirable, and as to such ordinary gases these elements can function satisfactorily, although their sensitivity in certain instances is not great. In the usual application such elements in order satisfactorily to support combustion upon their own surfaces must be heated, which heating can be accomplished by electrical means, or in different ways.

As to the resistant gases, an example being methane, or gas mixtures with air or oxygen in which methane predominates or is importantly present, the ordinary sensing agent is not sufficiently sensitive as to support surface or internal combustion when the mixture strength is below the "lower explosive limit," unless heated to a very high temperature.

The present invention is directed to the provision of a combustible gas sensing agent sufficiently sensitive as

to sense the presence of a resistant gas and air or oxygen mixtures below the "lower explosive limit," and also comprises a method by which an ordinary sensing agent may have its sensitivity and activity increased as to enable it so to function.

In use the sensing agent exposed to the mixture of combustible gas and air or oxygen includes a body or a mass in or on which the heavy metal is deposited. According to the present invention the method is as follows.

Step 1.—A body or mass of asbestos fibre or porous ceramic, including fire clays and unglazed porcelain materials, such as "sillimanite," or a metallic surface such as an electrical heater filament of Nichrome resistance wire, is formed by any conventional method into the desired shape of the sensing element. Such methods of formation include molding in liquid or dampened state and subsequent drying; stamping; pressing; shaping; or cutting to size from a larger body; it also includes all other conventional methods of forming asbestos fibre, porous ceramic, and resistance wire, or metals, into a desired shape or form. The term "resistance metal" is defined as a metal or alloy which becomes incandescent when a sufficient amount of electric current is passed through it, usually a nickel-chromium alloy.

Step 2.—The product of Step 1 is impregnated and/or coated with thorium oxide (ThO_2) as by precipitating the oxide into or upon the surface of the body or mass produced by Step 1. The precipitation is accomplished by moistening the product of Step 1 with a solution of thorium oxide and sulfuric acid, or with an aqueous solution of thorium nitrate, and effecting precipitation of the thorium oxide by heat.

Step 2(a).—Alternative to Step 2, the thorium oxide can be mixed with the ceramic material or asbestos fibre prior to Step 1. In this event the thorium oxide in powdered form is physically molded into the mass of material with which it is to be mixed.

Step 3.—The product of Steps 1 and 2, or 1 and 2(*a*), is heated to a temperature of incandescence to effect the firm integration of the thorium oxide therein and thereon.

Step 4.—A sensing agent from the platinum metals group comprising platinum or palladium with or without traces of iridium, osmium, ruthenium, and rhodium, permissibly present as impurities, is then deposited in finely divided form on, and within, the product of Step 3. Most all commercially available platinum and palladium solutions contain traces of one or more of the other metals of the platinum group. To effect this deposition the metal is precipitated from a solution of one of its salts, with which solution the product is moistened. As an example of this step, the double salt of platinum identified as platinic ammonium chloride, in aqueous solution, is precipitated on, and within, the product of Step 3 by the application of heat. Or, a solution of the salt of platinum identified as platinic chloride may be used in the same manner. In the case of palladium the metal is precipitated from a solution of the salt identified as palladium chloride by the application of heat.

Following the precipitation, the impregnated and coated product is ready for use.

Specific examples are as follows:

Example 1.—A mass of asbestos fibres weighing 5 milligrams shaped into a body about the size of a pin-head or larger is moistened with a solution of thorium oxide and sulfuric acid made by adding thorium oxide to concentrated sulfuric acid to form a saturated solution. The moistened mass is then heated until dry at approximately 700 degrees Fahrenheit and then heated to incandescence following which it is permitted to cool in the atmosphere. Platinum is then deposited on and within the mass by moistening the latter with an aqueous

Published by AsbestosClaims.Law
asbestosclaims.law/library/22083/1

saturated solution of platinic ammonium chloride and heating to incandescence. The aqueous solution held by the asbestos-thorium oxide mass thus heated to a temperature of incandescence until dry effects deposition of the metallic platinum. The product comprising asbestos fibres impregnated and coated with thorium oxide and platinum is then ready to be used. The exact amount of thorium oxide or platinum present is not important and the unit will operate so long as a "trace" or more is present although a longer operating life is obtained if more than a trace is provided.

Example 2.—A mass of porous ceramic material such as porcelain mixture weighing about 2 milligrams is molded into a body having a surface area of about pinhead size or larger and permitted to dry and harden. This body is substituted for the asbestos mass of Example 1 and is impregnated with thorium oxide and platinum and then heated as there described. The product comprises a ceramic body impregnated with thorium oxide and platinum.

Example 3.—A wire of Nichrome which may be of .002 inch diameter and 1 inch in length is wound or shaped as desired. This wire is substituted for the asbestos of Example 1 and is impregnated, or coated, with thorium oxide and platinum and then heated as there described. The product comprises a wire coated with thorium oxide and platinum.

Example 4.—In Example 1 an aqueous solution of palladium chloride, the concentration of which is not important but which may be a 5% solution, is used instead of platinic chloride.

Example 5.—In Example 2 a solution of palladium chloride, the concentration of which is not critical, 5% being suitable, is used instead of platinic chloride.

Example 6.—In Example 3 the solution of the salt identified as palladium chloride is used instead of platinic chloride.

Example 7.—A mass of asbestos fibres weighing about 5 milligrams is thoroughly mixed by moistening with distilled water with 1 milligram of powdered thorium oxide so that the asbestos fibers are completely mixed with thorium oxide. The mass is then compressed into a compact body about the size of a pinhead or larger and is heated to incandescence and permitted to cool in the atmosphere. Platinum is then deposited on and within the mass by moistening the latter with a saturated aqueous solution of platinic ammonium chloride comprising ammonium platinic chloride and distilled water. The asbestos and thorium oxide mass, moistened with ammonium platinic chloride solution is then heated to incandescence for one-half minute to effect deposition of the platinum and then removed and dried. The product is as in Example 1. Salts of palladium, as specified in the preceding examples, can be substituted for the platinic chloride.

Example 8.—A mass of porous ceramic material such as sillimanite, a porcelain mixture, weighing about 2 milligrams, is thoroughly mixed mechanically with 1 milligram of powdered thorium oxide. The admixture is then molded with water into any desired shape and permitted to dry. Thereafter the body is heated to incandescence and permitted to cool in the atmosphere. Platinum is then deposited on and within the mass by moistening the latter with a saturated aqueous solution of ammonium platinic chloride and heating to incandescence for one-half minute to effect deposition of the platinum and then removed. The product is the equivalent of that produced by Example 2. Salts of palladium with or without traces of iridium, osmium, ruthenium, and/or rhodium, can be substituted for the platinic chloride.

While this sensitizing process, which produces a hypersensitive sensing agent as here disclosed, makes the resultant element effective to sense resistant gas mixtures below the "lower explosive limit," it is not to be understood that the requirement of initial heat application to the sensing element in the conventional manner is eliminated when testing resistant gases. Such initial heat is usually necessary and can be applied by an electrically heated resistance element, in good heat transfer relationship with the sensing element. When functioning at ordinary room temperature it is frequently necessary to heat at least a portion of the element to a temperature of several hundred degrees Fahrenheit in order to effect the start of combustion within a small surface area of the element. The combustion over the remaining surface area will spread spontaneously thereafter.

It is to be understood that the exact density, concentration or amount of the thorium oxide, and of the sensing agent from the platinum group of metals, present in or on the sensing element made in accordance with the present invention, are not critical. The sensing element constructed as described and heated to within the range of 350 degrees Fahrenheit to 1800 degrees Fahrenheit will perform its sensing function so long as a trace of the thorium oxide and the sensing agent is present. The moistening may be accomplished in any conventional manner.

While the particular product and method herein disclosed in detail are fully capable of attaining the objects and providing the advantages hereinbefore stated, it is to be understood that they are merely illustrative of the presently preferred embodiments of the invention and that no limitations are intended to the details of construction, design, or process herein disclosed other than as defined in the appended claims.

I claim:

1. A combustible gas sensing element adapted to determine the presence of mixtures of combustible gas and air or combustible gas and oxygen, below the lower explosive limit, comprising a carrier of a material selected from the group consisting of asbestos, ceramic material, and nickel-chromium alloys, said carrier being impregnated with thorium oxide and a sensing agent selected from the group consisting of platinum and palladium.

2. The element of claim 1 in which the carrier is a nickel-chromium wire, and both the thorium oxide and the sensing agent are coated on the surface of the wire.

3. The element of claim 1 in which said thorium oxide and said sensing agent are precipitated on the carrier by moistening the carrier with a solution of their salts and then heating the carrier to incandescence.

4. The element of claim 1 in which the carrier is of asbestos.

5. The element of claim 1 in which the carrier is of ceramic material.

6. A combustible gas sensing element adapted to determine the presence of mixtures of combustible gas and air or oxygen below the lower explosive limit comprising a carrier of Nichrome wire impregnated with thorium oxide and having as a coating on the impregnated wire finely divided metal taken from the group consisting of platinum and palladium.

7. A combustible gas sensing element of the type described comprising a resistance wire coated with thorium oxide and platinum.

References Cited in the file of this patent

UNITED STATES PATENTS

612,614	Porter	Oct. 18, 1898
614,555	Killing	Nov. 22, 1898
980,802	Kreidl	Jan. 3, 1911
1,020,255	Bohm	Mar. 12, 1912
1,366,773	Duprac et al.	Jan. 25, 1921
2,079,404	Harris	May 4, 1937
2,478,916	Haensel et al.	Aug. 16, 1949
2,550,531	Ciapetta	Apr. 24, 1951
2,557,372	Cerulli et al.	June 19, 1951

FOREIGN PATENTS

1,535	Great Britain	of 1898

Published by AsbestosClaims.Law
asbestosclaims.law/library/22083/2