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GAS DETECTING APPARATUS

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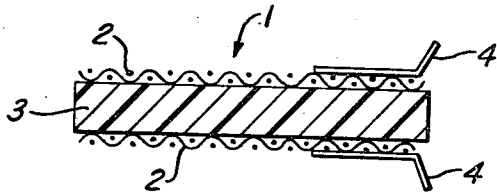


Fig. 1.

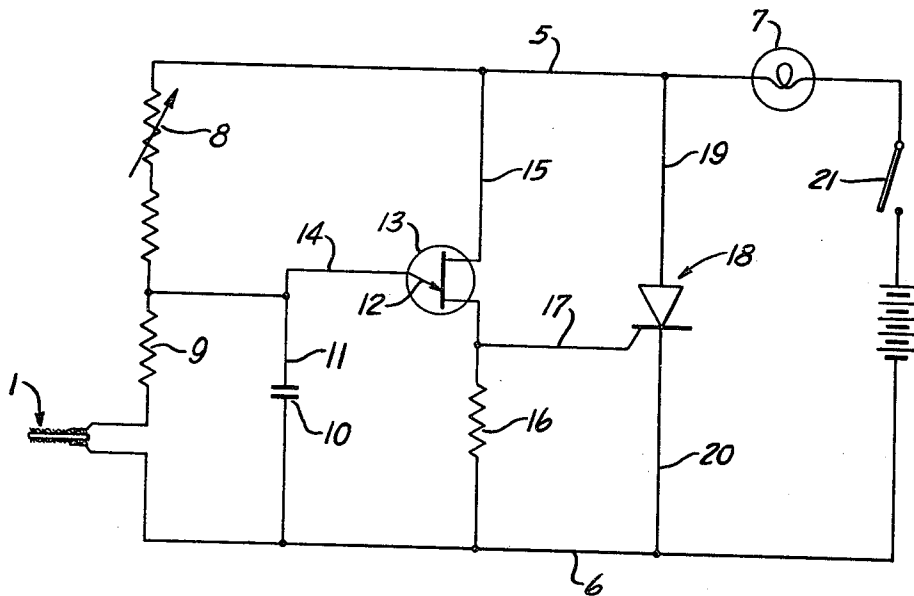


Fig. 2.

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## GAS DETECTING APPARATUS

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15 Claims

### ABSTRACT OF THE DISCLOSURE

A device for detecting the presence of an additive in a gaseous medium which includes a pair of spaced electrodes and a dielectric web is located between electrodes. An electrolyte is coated on the web and is adapted to conduct a current between the electrodes. The electrolyte includes a substance capable of reacting with the additive in the gas to form an insoluble reaction product. The reaction product precipitates to increase the resistance of the electrolyte and the increase in resistance serves to actuate a signalling device or alarm.

This invention relates to a gas detecting device and more particularly to a device for detecting the presence of hazardous gases and automatically energizing an alarm signal in the event the concentration of the gas exceeds a predetermined value.

Natural gas is used extensively for residential heating as well as in various industrial processes. The gas itself has very little, if any, odor and because of its explosive nature, additives, such as mercaptans are incorporated with the gas to provide the gas with a noticeable odor. While the mercaptan does provide some aid in detecting the presence of the gas, it is nevertheless desirable to have means for detecting the presence of gas resulting from leakage and to provide an alarm when the concentration of the gas in the atmosphere exceeds a given level.

The present invention is directed to an improved element for detecting the presence of gas based on the reaction of the constituents of the element with the mercaptan additives in the gas.

According to the invention the gas sensing element includes a non-absorbent, electrically insulating, fibrous web located between a pair of metal grids which serve as electrodes and are connected to a source of electrical energy as well as to an alarm signal. A solution of water and a water soluble humectant is coated on the fiber web and a metal salt is dissolved in the solution to form an electrolyte which is capable of conducting a current between the spaced electrodes. The salt is one which will form an insoluble sulfide on reaction with a mercaptan. In addition, an attractant can be added to the electrolyte and serves to increase the solubility of the mercaptan in the electrolyte. When gas is present, the mercaptan will dissolve in the electrolyte solution and react with the metal salt to form an insoluble metal sulfide which precipitates. The precipitate will increase the resistance of the electrolyte and a predetermined increase in resistance will energize the alarm, which can be a horn, light or the like.

The gas detecting unit of the invention is an extremely sensitive unit, based on the reaction of the metal salt in the electrolyte with the mercaptan in the gas to form an insoluble salt which thereby increases the resistance of the electrolyte. This increase in resistance acts through a control circuit to actuate an alarm which will notify the occupants of a dangerous increase in the level of gas in the particular area in which the detector is located. The alarm circuit is irreversible, meaning that once the alarm

is triggered, the circuit is permanently activated and the alarm will continue to be energized, regardless of any change in resistance of the sensing element, until the control circuit is manually opened. To reactivate the device it is necessary to substitute a new sensing element.

The gas detecting system of the invention is a small and inexpensive unit that can be used in the home as well as in industry to detect the presence of natural gas, water gas as well as other fuel gases containing mercaptan additives. Moreover, the device, by utilizing similar principles of operation, can be employed to detect the presence of other hazardous gases. In this situation, the electrolyte would include a dissolved constituent which would react either with the gas to be detected or an additive to the gas, to produce an insoluble reaction product, thereby increasing the resistance of the electrolyte to the flow of current.

Other objects and advantages will appear in the course of the following description.

The drawings illustrate the best mode presently contemplated of carrying out the invention.

In the drawings:

FIG. 1 is a side elevation of the gas sensing element of the invention; and

FIG. 2 is a wiring diagram of the control circuit incorporating the gas sensing element and an alarm.

The drawings illustrate a gas sensing element 1 which is to be connected in an alarm circuit to detect the presence of a gaseous component or additive in natural gas, water gas or the like. As natural gas has very little, if any, odor, an additive such as a mercaptan is added to the gas to provide a noticeable odor which can be detected in the event of gas leakage. The mercaptan which is added to the gas has the general formula,  $RSR'$ , with R being an alkyl group containing up to 4 carbon atoms, and R' being hydrogen or an alkyl group containing up to 4 carbon atoms. The common mercaptans which are added to the gas are ethyl mercaptan, methyl mercaptan, N-propyl mercaptan, iso-propyl mercaptan and N-butyl mercaptan. According to the invention, the element 1 is adapted to sense the presence of the mercaptan and thereby energize an alarm system to notify or signal the presence of an excessive quantity of the gas in the atmosphere.

The element 1 includes a pair of metal grids or electrodes 2 which are located on opposite sides of a web 3. Suitable terminals 4 are connected to each of the grids 2 and are connected in a control circuit to be described hereinafter.

The metal grids 2 serve as the electrodes for connection of the element 1 in the alarm circuit and can be formed of any common electrically conductive metal, such as bronze, copper, steel, aluminum, zinc, silver and the like. The grids 2 can either be in the form of screening or perforated plates, or metal foil can be used. It is preferred, however, to use a perforated type of grid, such as metal screening, so that the gas in the atmosphere can penetrate through the electrode and contact the web located between the electrodes. For most applications screening having from 40 to 120 strands per inch is preferred.

The web 3 serves as a carrier for an electrolyte and is formed of non-absorbent, electrically insulating material. The web can be formed of synthetic organic fibers, such as rayon, nylon, Dacron, Orlon or the like, or mineral fibers, such as glass and asbestos. The fibers can be in the form of haphazardly arranged fibers, as in paper or matting, or unidirectional fibers, or the fibers can be woven in the form of fabric or netting. As an alternative, the electrically insulating web 3 can be in the form of perforated sheeting rather than fibrous material and the perforated sheeting will serve as the carrier for the electrolyte which extends continuously between

the grids 2. It has been found that the sensitivity of the element decreases as the thickness of the web increases. However, if the web is too thin, the original resistance of the element will be below the desired level so that the thickness and density of the web is selected to provide a balance between sensitivity and original resistance. For most applications the web will have a thickness of about .001 to .100 inch.

The electrolyte, which is impregnated or coated on the material of the web 3, serves to conduct a current between the metal grids 2. The electrolyte is preferably a solution of water and a water soluble humectant. Water, if used alone as the electrolyte, will evaporate under conditions of low relative humidity, and the humectant, which absorbs water, insures the presence of a liquid electrolyte under all conditions of humidity and temperature. The humectant is a water soluble material having a relatively high boiling point, generally above 200° F. Examples of materials which can be used as the humectant are glycerin, beta-methyl glyceryl monochlorohydrin, N-hydroxyethyl lactamide, alpha-methyl glycerol, pentamethylene glycol, ethylene glycol, propylene glycol, sorbitol, polyethylenimine, polyethylene oxide, N-methyl-2-pyrrolidone, and the like.

The proportions or concentrations of the water and the humectant in the electrolyte are not critical and depend on humidity and temperature conditions. Under conditions of very low relative humidity, a portion of the water will evaporate so that the electrolyte will consist primarily of the humectant. Under conditions of high relative humidity, water will be absorbed by the humectant so that the proportion of water in the electrolyte solution can be greater than the humectant. Generally, it has been found that an electrolyte solution prepared with two parts of the humectant to one part of water under normal conditions of temperature and humidity, will provide a very satisfactory solution which can vary widely in concentration of water and humectant, depending on changes in temperature and humidity.

It is preferred to use distilled water in the electrolyte as the presence of dissolved salts or other impurities in tap water may result in the precipitation of compounds which could affect the accuracy or sensitivity of the element.

The electrolyte contains a dissolved metal salt which is formed of a metal, such as copper, zinc, mercury, cobalt, silver, antimony, germanium, manganese, nickel, strontium, thallium, tin, lead, iron, cadmium and the like, which will react with the sulfur of the mercaptan to form a sulfide which is insoluble in the electrolyte. The metal salt is soluble in water and soluble in the pure humectant and will thus remain in solution as the proportions of water and humectant vary with changes in humidity and temperature. Examples of metal salts which can be used in the electrolyte are cadmium acetate, chloride, formate, nitrate and sulfate; cobalt chloride, nitrate and sulfate; antimony chloride and tartrate; copper chloride, sulfate and lactate; silver nitrate; zinc chloride, nitrate and sulfate; tin chloride and sulfate, ferric acetate, chloride and nitrate; lead acetate and nitrate; mercuric acetate and nitrate; nickel acetate, chloride, formate and sulfate; and the like.

While all of the above mentioned salts can be used in the electrolyte, some of the salts provide better performance characteristics than others in that they are more soluble throughout the range of 100% water to 100% humectant, and some salts form metal sulfides which are less soluble than sulfides formed with other metal salts.

The concentration of the metal salt in the electrolyte depends on the particular salt used and the humidity and temperature conditions. It is important, however, that the concentration of the salt be substantially less than its saturation solubility in the electrolyte under the expected conditions of use so that the salt will not precipitate

under changes in humidity or temperature. It has been found that as little as 0.001 gram of the salt per 100 ml. of electrolyte can be employed and under most conditions, the metal salt is added to the electrolyte in a concentration of about 1 gram per 100 ml.

In addition to the metal salt, the electrolyte preferably contains an additive or attractant which serves to increase the solubility of the mercaptan in the electrolyte. The attractant is soluble in both water and the humectant and it is important that the attractant be non-ionic, as either the presence of an anionic or cationic material will affect the resistance characteristics of the element. In addition, the attractant should have a relatively high boiling point, generally over 200° F. Examples of materials which will increase the solubility of the mercaptan in the electrolyte and can be used in the invention are amino acids, such as glycine and alanine; amides such as adipamide, acetamide, and dimethyl acetamide; proteins and pertones such as egg albumin, and partially hydrolyzed lactalbumen; urea; and dihydroxyethylcyclohexane.

The concentration of the attractant in the electrolyte is not particularly critical. Generally, the attractant is used in the proportion of 0.01 to 30 grams per 100 ml. of electrolyte. An amount less than 0.01 gram per 100 ml. does not provide any appreciable effectiveness and the maximum concentration is governed by the solubility of the attractant in the electrolyte. In most cases, a concentration of about 10 grams of the attractant per 100 ml. is used.

It is also contemplated that a wetting agent can be employed in the electrolyte to improve the wetting of the web 3. The wetting agent to be used should be a non-ionic material which is soluble in both the water and the humectant. Specific examples of wetting agents which can be employed are as follows: polyethyleneoxy phenol, polyethylene glycol 400 monolaurate, dihydroxyethyl lauramide, nonyl phenol adduct of propylene oxide, and the like.

The concentration of the wetting agent in the electrolytic solution is not critical and the amount of the wetting agent can vary widely. Generally, up to 5 grams of the wetting agent per 100 ml. of the electrolyte can be used with a range of 0.005 to 0.25 gram per 100 ml. being preferred. If the concentration of the wetting agent is too great, above 5 grams per 100 ml., it may detract from the sensitivity of the element. The wetting agent aids in providing a more uniform continuous coating of the electrolyte on the web.

In some cases, it may also be desired to add a reducing agent to the electrolyte. The reducing agent is used when a metal salt is employed which can exist in two or more valence forms, as for example, cupric and cuprous, ferric and ferrous, stannic and stannous, and the like. The reducing agent serves to maintain the metal salt in the lower valence form. Generally, the sulfides of the lower valent form of a metal are less soluble than the sulfides of the higher valent form of the metal and thus it is desirable to maintain the metal in its lower valent form if possible.

Examples of reducing agents which can be employed are zinc hydrosulfite, hydroquinone, stannous chloride, phenothiazine and the like. If a metal salt is used, as the reducing agent it is imperative that the sulfide of the metal be insoluble in the electrolyte system. Thus, for example, salts of sodium and potassium should not be used as the reducing agent for the sulfides of these metals would be soluble in the system and would destroy the desired characteristics of the element.

The concentration of the reducing agent to be employed is not particularly critical and should be sufficient to either reduce the higher valent form of the metal salt to the lower valent form or to prevent oxidation of the lower valent form. Normally, the amount of the reducing agent employed is substantially less on a molar basis than the salt and a stronger reducing agent should be employed than the reduced form of the metal.

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In preparing the element 1, the electrolyte is applied to the web 3 in any desired manner such as dipping, brushing, spraying or the like. After application of the electrolyte, the web can be blotted, if necessary, to remove excessive quantities of the electrolyte. The impregnated web is then positioned between the metal grids and held in intimate contact with the grids by electrically insulating thread or other insulating fasteners or connectors.

The electrolyte, under normal conditions before being exposed to the mercaptan, provides a given resistance to the flow of current between the grids 2. This resistance may vary to some extent due to temperature and humidity changes. However, if gas is present in the atmosphere containing the mercaptan additive, the mercaptan will be absorbed in the electrolyte and react with the metal salt to provide an insoluble metal sulfide which precipitates and increases the resistance of the electrolyte. The resistance increase provided by the precipitation of the metal sulfide is substantially greater than the variations in resistance caused by changes in temperature and humidity, and when the increase in resistance increases beyond a predetermined level, an alarm or signal is automatically energized through a control circuit, thereby indicating the presence of a dangerous concentration of gas in the atmosphere.

The control circuit is shown in FIG. 2, and the gas detecting element 1 is connected by lines 5 and 6 to a battery or other source of electrical energy. A light bulb 7 is connected in line 5 and serves as an alarm signal when lighted to indicate the presence of an excess concentration of gas in the atmosphere. Other forms of signals such as a bell, horn or the like can be used in place of the bulb 7.

A variable resistance 8 and a fixed resistance 9 are connected in line 5, and a condenser 10 in line 11 is shunted across the resistance 9 and the sensing element 1. The line 11 is connected to the trigger electrode 12 of a uni-junction transistor 13 by line 14. When the transistor 13 is triggered, a low resistance path through the base electrodes of transistor 14 in line 15 is provided. A resistance 16 is connected in line 15 in series with the base electrodes of transistor 13. In addition a line 17 connects the line 15 with the cathode electrode of a silicon controlled rectifier 18 and when the rectifier fires, a circuit is closed through the anode and cathode which are connected by line 18 and 19 to the power lines 5 and 6, respectively.

When the resistance of the element 1 increases due to the precipitation of the insoluble sulfide the voltage will correspondingly increase and the condenser 10 will be charged to the same voltage. When the voltage increases to the firing voltage of the uni-junction transistor 13, the transistor will trigger to provide a low resistance path through its base electrodes. This permits almost full voltage to be applied through the gate to the cathode of the silicon controlled rectifier 18, thereby firing the rectifier which closes the circuit through lines 19 and 20. When the transistor 13 is triggered, substantially full voltage passes through the lamp 7 to thereby light the lamp and indicate a dangerous concentration of gas. The use of the silicon controlled rectifier 18 provides an irreversible circuit which will retain the lamp 7 in the lighted condition regardless of the voltage applied to the condenser 10. Thus the lamp or bulb 7 will remain lighted until the manual switch 21 is opened to remove the voltage through the lamp.

The following examples illustrate the manner of preparing the gas sensing element of the invention:

## EXAMPLE 1

An element was constructed by positioning non-woven polyester plastic matting, having a thickness of .002 inch and a density of 35 grams per square yard, between a pair of bronze screen grids containing 70 wires per inch.

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The plastic matting was treated with an electrolyte solution consisting of 66 ml. of glycerol, 34 ml. of water, 1 gram of cuprous chloride and 10 grams of acetamide. After blotting to remove the excess solution the resistance of the cell was measured before and after exposure to n-propyl mercaptan with the following results:

Time-seconds:	Resistance—10 <sup>6</sup> ohms
0	.9
5	.5
10	1.5
30	10.0
60	55.0
300	190.0

The element was connected to an alarm circuit designed to be activated by an increase in resistance to  $20 \times 10^6$  ohms and the alarm was triggered in slightly less than 40 seconds.

A similar element was also exposed to natural alkane gas containing about 1 p.p.m. of ethyl mercaptan and the resistance change was similar to that set forth above.

## EXAMPLE 2

A series of elements similar to that of Example 1 were prepared, except that pure copper mesh (100 strands per inch) was used for the grids and 1% of zinc hydro-sulfite was added to the electrolyte. Using the copper mesh grids and this electrolyte, various types and thicknesses of dielectric web were employed. More specifically, samples were prepared using polyester unwoven plastic mat having thicknesses of .0047 inch, .004 inch, .1003 inch, .1002 inch and .0013 inch with web densities of 80, 80, 45, 25 and 15 grams per square yard, respectively, and using nylon with a Dynel binder having a web density of 35 grams per square yard.

Testing of the resistance of these elements indicated that the elements were qualitatively equivalent, having original resistant values in the range of 1 to  $9 \times 10^6$  ohms. In sensitivity to ethyl mercaptan, the tests showed that the speed of reaction increased as the web thickness decreased.

## EXAMPLE 3

A series of elements were prepared similar to that of Example 1 except that the following materials, in the amounts indicated, were substituted for the glycerol of Example 1.

	Grams
Beta methyl glyceryl mono chlorohydrin	15
N-hydroxyethyl lactamide	15
Alpha methyl glycerol	15
Pentamethylene glycol	20
Ethylene glycol	10
Propylene glycol	15
Sorbitol	15
Polyethylene imine	15
Polyethylene oxide	10
N-methyl-2-pyrrolidone	10
1,4 dihydroxy ethyl cyclohexane	10

The resulting increase in resistance of the various elements on exposure to mercaptan-containing natural gas were qualitatively equivalent to those observed in Example 1.

## EXAMPLE 4

A series of elements similar to that of Example 1 were prepared except that the following metal salts, in the stated proportions, were substituted for the cuprous chlo-

ride with the amounts given in weight percent to volume of the water-glycerol solution:

	Percent
Lead acetate -----	1/2, 1
Copper bromide -----	5
Antimony trifluoride -----	1
Cadmium chloride -----	2
Zinc sulfate -----	2.5
Cobalt sulfate -----	1
Germanium difluoride -----	.25
Ferric chloride -----	1
Manganese sulfate -----	1.5
Mercuric acetate -----	1
Nickel acetate -----	.5
Silver fluogallate -----	4
Strontium bromide -----	1
Thallium acetate -----	1
Tin sulfate (ic) -----	2
Copper chloride (ic) -----	1

In each case the grids or mesh electrodes were constructed either from the metal present in the metal salt used or of a metal less active than the metal present in the salt.

In testing at 72% relative humidity and 70° F. the responses of the various elements after exposure to n-propyl mercaptan were qualitatively similar to the response described with respect to Example 1.

#### EXAMPLE 5

A series of elements were prepared using various mesh sizes of bronze screen. In accordance with these tests a polyester non-woven fabric was coated with an electrolyte consisting of 67 ml. of glycerol, 33 ml. of water, 1 gram of cuprous chloride and 10 grams of urea. Bronze screen having a mesh size of 150, 120, 70, 40, and 14 strands per inch was used in the various elements and the elements were all equilibrated at 60° F. and 80% relative humidity prior to testing.

In testing the resistance of the various elements, the original resistance increased as the mesh size was increased. It was also noted that the sensitivity to the mercaptan also increased with increased mesh sizes. Optimum combinations of original resistance and sensitivity were found in the range of 40-120 strands per inch.

#### EXAMPLE 6

An element, similar to that of Example 1, was prepared with the exception that 0.5 gram of stannous chloride was added to the electrolyte. On exposure to ethyl mercaptan a momentary decrease in resistance occurred, probably due to the formation of hydrochloric acid, and this was followed by an extremely rapid increase in resistance from an original value of  $1.5 \times 10^6$  ohms to  $600 \times 10^6$  ohms.

#### EXAMPLE 7

An element was prepared by dissolving 1 gram of thallium acetate and 10 grams dihydroxyethyl cyclohexane in 100 ml. of a solution consisting of 67 parts of glycerol and 33 parts of water, and containing 0.5 gram per 100 ml. of polyoxyethylene p-nonyl phenol. The solution was then impregnated on .002 inch polyamide resin random, non-woven fabric such that the electrical resistance of a 1/2" x 1/2" section tested between two silver screen electrodes (60 strands per inch) at a temperature of 70° F. and 72% relative humidity was  $1 \times 10^6$  ohms. Upon exposure to n-propyl mercaptan at a concentration of approximately 1 p.p.m., the resistance increased to a value of  $30 \times 10^6$  ohms in a period of 4 minutes.

#### EXAMPLE 8

An element similar to that of Example 7 was prepared substituting zinc sulfate for the thallium acetate and substituting adipamide for the dihydroxyethyl cyclohexane. When tested between similar silver screen electrodes in a

similar manner the resistance increased from a value of  $1 \times 10^6$  ohms to  $30 \times 10^6$  ohms in a period of 3.5 minutes.

#### EXAMPLE 9

A sensing element similar to that of Example 7 was prepared, except that lead acetate was substituted for the thallium acetate and partially hydrolyzed casein was substituted for the dihydroxyethyl cyclohexane. The resistance of the sensing element increased from an original value of  $1 \times 10^6$  ohms to  $30 \times 10^6$  ohms in a period of 4 minutes.

#### EXAMPLE 10

A sensing element similar to Example 7 was prepared except that lead acetate was substituted for the thallium acetate and N-methyl-2-pyrrolidone was substituted for the dihydroxyethyl cyclohexane. The resistance of the element increased from an original value of  $1 \times 10^6$  ohms to a value of  $30 \times 10^6$  ohms in a period of 2 minutes.

The gas sensing unit of the invention is an inexpensive, highly sensitive unit which is capable of detecting the presence of a predetermined concentration of a hazardous gas. As described above, the dissolved metal salt reacts with the mercaptan in the gas to provide an insoluble sulfide which increases the resistance of the sensing element. It is contemplated that the unit can also be employed to detect the presence of other hazardous gases or additives to gases. In the case of other gases, the electrolyte contains a soluble constituent which is capable of reacting with the gas to be detected, or with an additive to the gas, to form an insoluble reaction product. The precipitation of the reaction product will increase the resistance through the sensing element in the manner previously described. The gas sensing unit can be employed to detect the presence of warfare gases such as phosgene, cyanide gases such as may be used in metal processing industries, carbon monoxide such as generated from internal combustion engines or in nickel recovery plants, dry cleaning vapors or solvents, and the like.

Various modes of carrying out the invention are contemplated as being within the scope of the following claims particularly pointing out and distinctly claiming the subject matter which is regarded as the invention.

We claim:

1. A device for detecting the presence of a mercaptan additive in a gaseous material, comprising a pair of spaced electrodes, a dielectric web disposed between the electrodes, an electrolyte solution coated on the web and extending continuously between the electrodes and adapted to conduct a current between said electrodes, said electrolyte including a substance dissolved therein and capable of reacting with the mercaptan to form an insoluble reaction product, said reaction product precipitating to vary the resistance of the electrolyte, means for connecting the electrodes in an electrical operating circuit with a signalling device and a source of power, said circuit being arranged so that the current supplied to the signalling device is normally less than that required to operate said signalling device, and means responsive to a given variation in resistance of the electrolyte to increase the magnitude of the current supplied to the signalling device to thereby energize the signalling device.

2. The device of claim 1, and including means for preventing the deenergization of the signalling device until the operating circuit is manually opened.

3. An element for detecting the presence of a mercaptan additive in a gaseous medium, comprising a pair of spaced metal electrodes, an electrically insulating fibrous web disposed between the electrodes, and an electrolyte impregnated on the fibers of the web and extending continuously between the electrodes, said electrolyte capable of conducting a current between the electrodes and having a given resistance under predetermined conditions of temperature and humidity, said

electrolyte comprising a solution of water and a water soluble humectant and said electrolyte having dissolved therein a compound capable of reacting with the mercaptan additive in the gaseous medium to form an insoluble reaction product, said reaction product precipitating to increase the resistance of the electrolyte and thereby energize a signalling device.

4. The element of claim 3 in which the electrolyte has dissolved therein a material characterized by the ability to increase the solubility of said gas additive in said electrolyte, said material being soluble in both the water and the humectant.

5. The element of claim 3 in which the metal salt has a concentration substantially less than the saturation solubility of the salt in the water-humectant solution under the conditions of use and greater than .001 gram per 100 ml. of the water-humectant solution.

6. The element of claim 3 in which the metal electrodes have an open construction whereby the gaseous material can freely pass through the electrodes and contact the web located therebetween.

7. The element of claim 3 in which the electrodes are metal screens with said screens having from 40 to 120 threads per inch.

8. The structure of claim 3 in which the solution comprises about 2 parts of humectant and 1 part of water at a temperature of 70° F. and 70% relative humidity.

9. The element of claim 3 in which the humectant is selected from the group consisting of glycerin, beta-methyl glyceryl monochlorohydrin, N-hydroxyethyl lactamide, alphanmethyl glycerol, penta-methylene glycol, ethylene glycol, propylene glycol, sorbitol, polyethylenimine, polyethylene oxide, N-methyl-2-pyrrolidone, and mixtures thereof.

10. An element for detecting the presence of a mercaptan additive in a gaseous medium, comprising a pair of spaced metal electrodes, an electrically insulating fibrous web disposed between the electrodes, an electrolyte impregnated on the fibers of the web and extending continuously between the electrodes, said electrolyte capable of conducting a current between the electrodes and having a given resistance under predetermined conditions of temperature and humidity, said electrolyte comprising a solution of water and a water soluble humectant and having dissolved therein a metal salt, said metal salt being soluble in both the water and the humectant and being capable of reacting with the mercaptan additive in the gas to form an insoluble reaction product, said reaction product precipitating to vary the resistance of the electrolyte, and a substance dissolved in said electrolyte, said substance being soluble in both the water and the humectant and characterized by the ability to increase the solubility of the mercaptan additive in the electrolyte.

11. The element of claim 10 in which said substance has a concentration in the range of .01 to 30 grams per 100 ml. of the water-humectant solution.

12. The element of claim 10 in which the metal of the salt is selected from the group consisting of zinc, copper, mercury, cobalt, antimony, germanium, manganese, nickel, strontium, thallium, tin, lead, iron, silver, cadmium, and mixtures thereof.

13. An element for detecting the presence of a mercaptan additive in a gaseous medium, comprising a pair of metal electrodes of open construction, a fibrous web disposed between the metal electrodes and formed of a

series of a dielectric filament, an electrolyte impregnated on the surface of the web and extending continuously between the electrodes, said electrolyte comprising a solution of water and a water soluble humectant and having dissolved therein a metal salt, said electrolyte being capable of conducting a current between the electrodes and having a given resistance in the absence of said additive, said salt being soluble in both the water and the humectant and capable of reacting with the mercaptan additive to form an insoluble reaction product, said reaction product precipitating in the electrolyte to vary the resistance of the electrolyte and thereby energize a signalling device, said metal salt being present in a concentration substantially less than saturation solubility of the salt in the water-humectant solution under the expected conditions of use.

14. An element for detecting the presence of a mercaptan additive in a gaseous material, comprising a pair of spaced electrodes, a dielectric web disposed between the electrodes, an electrolyte coated on the web and extending continuously between the electrodes, said electrolyte capable of conducting a current between the electrodes and having a given resistance under predetermined temperature and humidity conditions, said electrolyte having dissolved therein a metal salt capable of reacting with the mercaptan to form an insoluble reaction product, the metal of said salt characterized by the ability to exist in two valence forms, said reaction product precipitating to increase the resistance of the electrolyte and said increase in resistance serving to actuate an alarm, and a non-ionic reducing agent dissolved in the electrolyte, said reducing agent reducing said metal to its lower valent form in the electrolyte.

15. A device for detecting the presence of a gaseous material containing an alkyl mercaptan, comprising a pair of spaced electrodes, a dielectric fibrous web disposed between the electrodes, an electrolyte coated on the fibers of the web and extending continuously between the electrodes and adapted to conduct the current between the electrodes, said electrolyte comprising a solution of water and a water soluble humectant and said electrolyte having dissolved therein a metal salt capable of reacting with the mercaptan in the gas to form an insoluble metal sulfide, said metal sulfide precipitating to increase the electrical resistance of the electrolyte, means for connecting the electrodes in a control circuit including a signalling device, and means responsive to a given increase in the electrical resistance of the electrolyte to energize the signalling device.

#### References Cited

##### UNITED STATES PATENTS

2,517,382	8/1950	Brinker et al. ....	204—195
2,851,411	9/1958	Bly .....	204—195
2,862,859	12/1958	Grosskopf .....	204—1.1
3,028,317	4/1962	Wilson et al. ....	204—1.1
3,029,384	4/1962	Hart .....	204—195
3,205,158	9/1965	Renier .....	204—195
3,337,441	8/1967	Goldsmith .....	204—195
3,338,812	8/1967	Dworak et al. ....	204—195

T. TUNG, Primary Examiner

U.S. Cl. X.R.

204—1