Jan. 29, 1957 C. C. ANTHES 2,779,666

HALIDE DETECTOR

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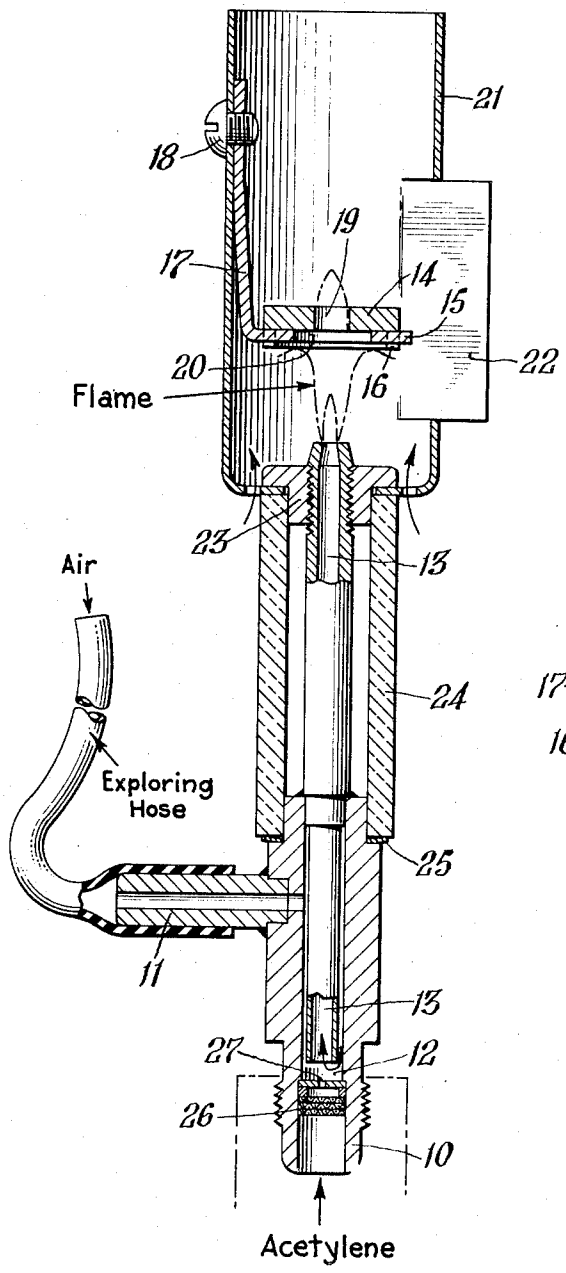


Fig. 1.

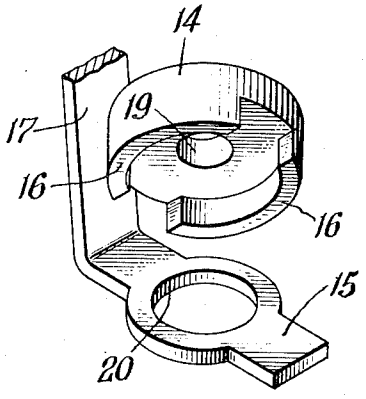


Fig. 2.

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HALIDE DETECTOR

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8 Claims. (Cl. 23—254)

This invention relates to a halide detector such as is used for the discovery of leaks around domestic and commercial refrigerators using a halide gas in common practice today. An object of this invention is to enhance the sensitivity of the detector. Another object is to prolong its life before renewal of a copper-containing reaction disc becomes necessary. A further object is to provide a detector of this sort which is more convenient to handle for a prolonged period without becoming objectionably hot to the hand.

Heretofore, a commercial detector of this sort has been of the general type disclosed in the patent to Tuel No. 2,200,523, dated May 14, 1940 and entitled Gas Detector. This prior device has a flame nozzle to which a fuel gas is supplied under pressure for aspirating air to a flame nozzle for directing a flame through a perforate disc of copper. A light and wind shield of cylindrical shape encloses the flame and reaction disc. When a halide gas in suitable proportions is mixed with the aspirated air, the flame issuing from the copper reaction disc becomes a distinctive color indicating the presence of a halogen or compound thereof in the air supplied in concentrations of about 150 parts of the halide gas per million parts of air and stronger concentrations of the halide.

According to this invention it has been discovered that a stainless steel reaction disc beside the one of copper is able to impart a different and distinctive yellowish color to the flame at concentrations of the halide gas far below those for which the copper disc alone is able to provide an indication. The stainless steel disc is about 1000% more sensitive and able to detect the presence of a halide at concentrations of about 15 parts per million parts of aspirated air. Thus the stainless steel disc functions at concentrations of the gas being sought, well below those for which the copper has been found sensitive. In event that the halide content of the supplied air rises to a value strong enough for the copper disc to function as an indicator, the copper disc takes over, masking the yellowish color with a bluish green, which turns to a purple with still stronger halide concentrations.

Where the former copper disc had an average life of perhaps 14 hours, it has been discovered that by using a reaction plate of silicon copper its life may be prolonged about seven times that of the prior copper plate.

Referring to the drawing, Fig. 1 is a longitudinal section through a preferred embodiment of this invention. Fig. 2 is a perspective showing how the two reaction discs of Fig. 1 fit together.

As shown in Fig. 1, the device illustrated is provided with a fuel gas inlet connection **10** and an air connection **11**. Any one of a number of fuel gases may be used, such as acetylene, natural gas, and many others, and advantageously the gas selected can be among the less expensive types. Air is aspirated by the fuel gas into the mixing chamber **12** from which a passageway **13** extends to a usual type flame nozzle. The flame may be of any conventional shape and preferably is fairly colorless for the flame color tests and may be of the general shape illustrated by the dotted lines of Fig. 1 of the drawing. A copper containing disc **14** receives the direct impact of the flame upon it and a stainless steel disc **15** is held contiguous the disc **14** by a flange **16** on the disc **14**, which flange is crimped over to hold the discs **14** and **15** together.

In Fig. 2, the shape of these discs will be apparent from the drawing, the disc **14** has a groove through its flange **16** and extensions on the disc **15** project in the groove through the flange.

A supporting arm **17** of stainless steel, at one end of which the disc **15** as formed, is provided with a sharp bend as illustrated and a screw **18** secures this arm **17** for supporting these discs from the usual light and wind shield **21** illustrated as being of generally cylindrical shape and extending around the flame, to make color changes in the flame more readily perceptible and to prevent drafts distorting the flame. The copper-containing disc **14** is provided with a perforation **19** substantially coaxially aligned with the flame nozzle, while the disc **15** has a larger perforation **20** also coaxial as illustrated.

The light and wind shield **21** is provided with a window **22** through which the flame may be viewed. A bushing **23** is provided with the flange illustrated, against which the shield **21** may be held by a thermally insulating sleeve **24** held in place by the spring **25** illustrated. The tube walls around the passageway **13** within the sleeve **24** are of stainless steel to reduce heat conduction to the main body portion of the inlet connections **10** and **11**.

Discs of screening material **26** serve to filter out any foreign matter in the fuel gas before such gas passes through the orifice **27** creating a sub-atmospheric pressure in the mixing chamber **12**.

In operation the detector of this invention may be used in substantially the same way as is contemplated for that in the Tuel patent mentioned above, No. 2,200,523. One way in which the device may be operated is to move the air intake hose illustrated up and down and around a commercial or domestic refrigerator or the like in an effort to discover possible leakage of the refrigerating gas containing halogenated hydrocarbons. When concentrations of halogen containing gas in at least 150 parts per million parts of air, or stronger are discovered the flame issuing from the reaction discs will be colored a light blue, turning, with strong concentrations, to a purple.

According to one phase of this invention it has been discovered that, when an ordinary 18–8 stainless steel disc commercially designated as the type 304 and containing a very small amount of sodium in presumably non-volatile form at a dull red heat is placed beside a copper disc in the manner illustrated, this detector becomes about ten times more sensitive to the presence of halides in the air. In concentrations of gas containing a halogen or compounds thereof of at least about the strength of 15 parts per million parts of air a yellowish color is discernible in the flame due to the presence of the halide gas and the stainless steel disc. In concentrations between the aforementioned minimum of about 15 parts per million and the concentration at which a copper containing disc begins to function, i. e. about 150 parts per million, the stainless steel disc of this invention provides the new and more sensitive detector by flame color for the presence of halide compounds in the gas. As the concentration of halide gas increases in strength the effect is at first a blending of the colors due to the flame indication from each disc. This blending is at first a light blue. Later with increasing concentrations the color from the copper containing disc becomes dominating and substantially masks the color due to this stainless steel.

Another use for the detector of this invention is in

connection with a test of a vacuum chamber where halogen containing compounds may be placed around the outside of the chamber and the detector of this invention used in connection with the exhaust gases from a vacuum pump exhausting the chamber, the gas tightness of which is being tested.

In operation it has been found that the best results were obtainable with the discs of the approximate shape illustrated. Due to the copper containing disc 14 being a better conductor of heat, it was found the flame should impinge upon the side of the disc 14 around its central orifice for a substantial area to supply heat conducted away from the inner portion of the disc 14. The stainless steel disc 15 being much less thermally conductive than the disc 14 did not seem to need so much heat applied to it except closely around its perforation. It is estimated that both discs were brought to a dull red heat around their perforations. Perhaps the average temperature of each disc was in the neighborhood of 1100° F. to 1500° F. The precise temperature of the disc does not appear to be critical.

A noteworthy feature of this invention is the use of a supporting arm 17 of stainless steel whereby the poor thermal conductivity of the stainless steel enables less heat to be transmitted to the light and wind shield 21. Another worthwhile feature of the apparatus illustrated is the use of thermal insulating material 24 providing a convenient handle grip for an operator.

A number of different batches of type 304 stainless steel from different manufacturers were tried and all found to be about equally suitable as a sensitive indicator of the presence of halides. A typical formula for this type 304 stainless steel has the following maximum values reported by the manufacturer for the elements mentioned: .08% carbon; 2.00% manganese; 1.00% silicon; .04% phosphorus; .03% sulphur; 18.00% to 20.00% chromium; 8.00% to 11.00% nickel and the balance iron. The necessary presence of sodium in non-volatile form at a dull red heat was not reported.

A visual spectograph analysis of the yellow color due to the reaction of the halide containing gas with the stainless steel proved by the wave length of the color tested that such distinctive yellow color was due to the presence of sodium. At first on heating, the yellow color was present, showing that traces of sodium probably in volatile form at the temperature of dull red heat, were present without any halide in the flame. This volatile sodium burned off in about a minute leaving no indication of any more sodium being present in the stainless steel. On the presence of a member selected from the group consisting of halogens and halides in the air and flame, the yellow colored flame again appeared indicating sodium. As the presence of the halide gas continued the stainless steel reaction disc gave the sodium yellow colored flame. However, on continued use it was noted the disc became less sensitive to the halide gas. It was found that knocking or jarring the stainless steel disc resensitized it. This was found to be due to the formation of a metal oxide coating on the surface at the dull red heat, and this oxide coating was so untenacious that it was easily jarred off.

Efforts to determine how small the traces of sodium in non-volatile form may be have so far been inconclusive. It is believed that sodium in very small quantities in steels has been extremely difficult if not impossible of quantitative determination. This is confirmed by the literature which gives compositions of steel alloys to one one hundredth of a percent for many of the elements but makes no mention of sodium. The analysis given above for the 304 type of stainless steel was taken from data supplied by a steel manufacturer. This mentions carbon, phosphorous, and sulphur to hundredth of a percent. Yet traces of sodium have been proven to be present when the yellow color is present without a halide present and again after this probably volatile sodium has been burned off, further sodium is shown to have been present as an indicator of the presence of a halide in the concentration range mentioned.

Many metals show traces of sodium capable of reacting with weaker concentrations of halide gas than can be indicated by the copper of prior art halide indicators. The field of possibly usable sensitive indicators is believed to be very large because most metals are believed to contain traces of both volatile and non-volatile sodium at the dull red heat. For example many types of non-corrosive steel alloys were tried and found suitable at first. Likewise many bronzes and brasses. Among metals which have not been found appropriate may be mentioned electrolytic iron, because of its extreme purity. The prior art copper does not show a yellow sodium flame with weaker concentrations. Aluminum is not appropriate for use as the reaction disc because it melts at too low a temperature. It therefore is believed that an essential of an equivalent of the type 304 stainless steel mentioned is that it must have a fusion temperature well above the 1500° F. mentioned above as a possible limit for a dull red heat. Another essential appears to be the possession of at least traces of non-volatile sodium, which must be present to react with the halide or in the presence of a halide and give the yellow color. One reasonable theory is that this non-volatile sodium material may be a sodium oxide. Text-books show such oxide to sublime at a temperature between 2300° F. and 2400° F. By increasing the flame temperature using oxygen and acetylene and raising the temperature of the reaction disc its sodium content that was not volatile as the dull red heat showed the sodium yellow without any halide gas supplied to the flame. It seems reasonable to conclude that such was due to the sodium that was non-volatile at the dull red heat becoming gaseous at the temperatures above 2400° F.

Another essential for a commercial equivalent of the type 304 stainless steel is an ability to retain its sensitivity. Many steels and other metals possessing traces of sodium that is non-volatile at a dull red heat and having a fusion temperature well over 1600° F. were found to be sensitive to halides for only a short time. The reason appears to be because a tenacious oxide coating forms at the dull red heat which appears to blanket the non-volatile sodium at such temperature. Commercially pure iron is such an example. Traces of the non-volatile sodium after the volatile sodium had been burned off at the dull red heat were appropriately sensitive to the halides but its sensitivity did not last. Even the preferred material, the type 304 stainless steel was not free from this handicap of losing its sensitivity. But the oxide coating on this type 304 stainless steel was fortunately found to be untenacious and capable of being jarred or knocked off easily. Removal of the oxide coating had the effect of renewing the sensitivity of the sodium bearing metal to the halide gas. Hence an easily removable oxide coating is a desirable characteristic. One possible reason why some oxide-metal coatings are untenacious is that the presence of internal stresses due to unequal thermal expansion in the oxide and metal overcome the binding action of the coating. Again the permeability of the oxide coating may affect the sensitiveness of the halide for the non-volatile sodium. The lack of sensitivity due to the absence of non-volatile sodium was largely overcome by impregnating the metals with sodium, by heating the metals with a 5% sodium mercury amalgam in an inert atmosphere and actually fusing the metals (copper at 2400° F. and stainless steel at 2800° F.) and allowing the fused metals to solidify in the inert atmosphere.

No proof is available that the impregnated sodium becomes oxidized but it is thought that may be the case. At any rate this impregnation is believed to get more sodium into the metal and with such a greater quantity of non-volatile sodium the metal is not believed to become desensitized as rapidly by an oxide coating at the dull red heat.

Next to the type 304 stainless steel mentioned above, a

desirable material found for the reaction disc **15** is a 25–20 stainless steel known commercially as type 310. A typical formula for the type 310 stainless steel is reported by the manufacturer to be as follows: .25% carbon; 2.00% manganese; 1.50% silicon; 24.00% to 26.00% chromium; 19.00% to 22.00% nickel and the balance iron. It is believed that substantially all stainless steels or non-corrosive steels having the small amount of non-volatile sodium at the dull red heat should function to give a sensitive indication of the presence of a halide gas in low concentrations. With some such steels it was noticed that the the sensitivity decreased as an oxide coating was formed, the sensitivity being restored upon scraping off the oxide coating. Some stainless steels such as the types 304 and 310 mentioned possessed an untenacious oxide coating of such character that it fell off with silght jars or impacts, without the necessity for actually scraping off such coating. The stainless steel disc appears to have a very long life, dependent only upon the length of use and the loss in metal from the oxidation referred to above.

Another feature of this invention resides in the copper containing disc **14**. To prolong the life of the copper disc around seven or eight times what its life formerly was, it has been found that an alloyed copper such as silicon bronze sold by American Brass Company under the designation 1012 not only has the longer life refered to, due probably to the slower oxidation of the copper, but that this slower oxidation does not affect the sensitivity of the copper to the presence of halide gases. A typical formula for the particular copper containing disc referred to is reported by the manufacturer to be as folows: 95.6% copper; .40% lead; 3.00% silicon; and 1.00% manganese. More specifically in this invention the disc **14** has been found to have an effective life of slightly over 100 hours before another disc of the same material should be substituted. Without any halide gas present in the flame, the only color discernible is that due to the flame itself, which is a very pale blue or almost colorless appearance.

The temperature of the discs is not believed to be critical so long as they are at least at a dull red color mentioned, however, their temperatures should not be near that at which either of the discs may fuse. The flame is that of an ordinary pre-mixed flame having an inner cone as illustrated and preferably also as nearly colorless as is reasonably obtainable.

It was found that National Bureau of Standards standard sample 123A of 18–11 stainless steel did not give a satisfactory halide indication. Another portion of the same sample melted down and prepared in the same manned but treated with a small amount of aforementioned sodium amalgam gave a good indication.

In this last case 20 grams of sample 123A was treated with .01 gram of the 5% sodium amalgam before melting.

Pure copper and also electrolytic iron impregnated with sodium in a similar manner gave like results. Not all metals have been tried out but it is believed that all metals having a melting point high enough to be satisfactory and an untenacious oxide coating could be impregnated with small amounts of sodium to possess the same in non-volatile form at a dull red heat to give satisfactory indications of halogen or halogen compounds in low concentrations. The sodium content should not be large enough to give a persistent yellow flame in the absence of a halide. The sodium content should be large enough to give a steady indication of a halide when the halide content is as low as about 15 parts per million. By having the copper containing reaction disc impregnated with sodium in the aforementioned manner it is not necessary to have a stainless steel disc. When only one reaction disc of sodium impregnated copper is used, it may be mounted in any convenient manner and secured to the shield **21**. Copper impregnated with a little sodium in form that is non-volatile at a dull red heat has the advantage of not appearing to become desensitized by an oxide coating that needs to be jarred or scraped off. Electrolytic iron impregnated with said sodium amalgam gave a satisfactory test. The metals that were impregnated with sodium to be in non-volatile form at a dull red heat seem to become desensitized to a less extent by an oxide coating. The reason for this is not known. The inert gas used was argon. Perhaps the sodium was impregnated into the metal in metallic form and then became oxidized or otherwise rendered non-volatile at the dull red heat, by uniting with oxygen in the air or elsewhere, or by uniting with some unknown material to render it non-volatile at that temperature. Possibly it is the greater quantity of non-volatile sodium that is responsible for the lessened appearance of a metal becoming desensitized by an oxide coating.

I claim:

1. In a halide detector having a flame nozzle, a metal reaction member adjacent said nozzle for being heated thereby, a fuel gas connection to said nozzle, and a connection for introducing air to said nozzle, said nozzle being of the type for heating said reaction member to a dull red heat with a substantially colorless flame, the combination therewith of the improvement for enhancing the sensitivity of said detector, said improvement including said reaction member having a small amount of sodium in non-volatile form at a dull red heat in quantity to give no yellow color to a flame from said nozzle in the absence of a gas selected from the group consisting of halogens and halides in air supplied to said flame after any volatile sodium has been burned off at said dull red heat, but in quantity large enough to give a yellow color to said flame at said dull red heat when a gas selected from the group consisting of halogens and halides is present in about at least 15 parts per million parts of air by volume, said reaction member forming at said dull red heat an untenacious metal oxide coating, and said metal reaction member having a melting temperature well above about 1600° F.

2. In a halide detector having a flame nozzle, a metal reaction member adjacent said nozzle for being heated thereby and containing no non-volatile sodium at a dull red heat, a fuel gas connection to said nozzle, and a connection for introducing air to said nozzle, said nozzle being of the type for heating said reaction member to a dull red heat with a substantially colorless flame, the combination therewith of the improvement for enhancing the sensitivity of said detector, said improvement including another metal reaction member adjacent the first to be heated by said flame nozzle and having sodium in non-volatile form at said dull red heat in quantity to give no yellow color to a flame in the absence of a gas selected from the group consisting of halogens and halides in air supplied to said flame after any volatile sodium has been burned off at said dull red heat but to give a yellow flame at said dull red heat when gas selected from the group consisting of halogens and halides is present in at least about 15 parts per million parts of air by volume, said second mentioned reaction member forming at said dull red heat an untenacious metal oxide coating and having a melting temperature well above 1600° F.

3. A detector according to claim 2 in which said first reaction member is a copper silicon alloy and said second reaction member is a chromium-nickel stainless steel alloy.

4. A detector according to claim 2 in which said second reaction member is a stainless steel containing traces of sodium in non-volatile form at a dull red heat.

5. A detector according to claim 2 in which said first reaction member is largely of copper, in disc form provided with a perforation substantially axially aligned with said nozzle, and said second reaction member is a disc contiguous the first reaction member, between said first reaction member and said flame nozzle, and provided

with a coaxial perforation larger than that in said first reaction members.

6. A detector according to claim 5 in which a light and wind shield is provided around said nozzle and reaction members, the first such member has a flange around a substantial part of the second reaction member, and a support of less thermal conductivity than that of said first reaction member is secured to said shield.

7. A halide detector comprising a metal reaction disc having a fusion temperature well above 1600° F., a flame nozzle for heating said disc to a dull red heat with a substantially colorless flame, a supply connection for fuel gas to said nozzle, means for aspirating air to said fuel gas, and means for controlling the supply of fuel gas to said nozzle, the combination therewith of the improvement for enhancing the sensitivity of said detector to the presence of a gas selected from the group consisting of halogens and halides in said aspirated air and fuel gas, said improvement including at least a trace of sodium in non-volatile form at a dull red heat in said disc.

8. A bi-metallic reaction disc unit for a halide detector comprising a copper alloy disc containing no non-volatile sodium at a dull red heat and a stainless steel alloy disc containing traces of sodium in non-volatile form at a dull red heat, said copper alloy disc having a peripheral flange crimped over a peripheral portion of the stainless steel disc with the central portion of each disc perforate, the perforate portion of the stainless steel disc being larger than the perforate portion of the copper alloy disc, and a supporting arm from the stainless steel disc by means of which said unit may be carried by

and secured to a light and wind shield around a detector flame, said stainless steel disc being of approximately an 18–8 type containing about .08% carbon, 2.00% manganese, 1.00% silicon, .04% phosphorous, .03% sulphur, 18.00% to 20.00% chromium, and 8.00% to 11.00% nickel, and the balance iron.

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