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DETECTION OF ALCOHOLS IN GAS ATMOSPHERES

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4 Claims

ABSTRACT OF THE DISCLOSURE

A method of detecting alcohols in air in accordance with which the air is passed into contact with a reagent consisting essentially of a soluble hexavalent chromium compound and a pentavalent phosphoric acid supported by an inert carrier. In the presence of an alcohol the reagent undergoes a color change which affords a qualitative determination of the presence of alcohol. Quantitative determination is possible by mounting the reagent in a transparent tube and determining the length over which the color change occurs upon passing a fixed volume of air at a fixed flow rate through the tube, the length over which the color change occurs being compared with calibrated results.

A variety of alcohols are used as solvents, in the manufacture of a large number of other compounds, in toilet and other preparations, and for various other purposes. Many of these alcohols are capable of causing dermatitis; the vapors of others in air may be hazardous to humans, exhibiting varying toxicity ranging from relatively harmless to definitely hazardous depending on the particular alcohol and the concentration present in the air being breathed. Also some alcohols when present in air present a fire or explosion hazard.

It is among the objects of this invention to provide a simple, rapid and reliable method of detecting the presence of alcohols in air, that may be practiced by non-technical persons, that is rapid, that is satisfactory for plant, field and laboratory use, that requires only simple, inexpensive and readily available materials and apparatus, and that is applicable to quantitative determinations.

A copending application Ser. No. 460,479, filed June 1, 1965, by Charles A. Plantz and David G. Hannan, and assigned to the owner of this application, discloses and claims a reagent for the detection of hydrazine, volatile alkyl hydrazines, red fuming nitric acid, etc., which comprises a composition of a hexavalent chromium compound and an acid of pentavalent phosphorus on an inert carrier which in the presence of moisture undergoes a characteristic and easily observable color change promptly upon contact with the said compounds.

I have discovered, and it is upon this that the present invention is predicated, that the aforesaid reagent is especially adapted to the practice of the method of this invention. In accordance with it the reagent is disposed within a transparent container and the atmosphere to be tested is passed through it. When an alcohol is present the reagent changes from its normal yellow color to green. This was unexpected because there is no chemical relationship between the foregoing nitrogen compounds and alcohols.

Satisfactory response of the reagent to the presence of alcohols is had by passing the atmosphere, as by an aspirator or a pump, to be tested through the reagent in the container. When used with gas mask canisters a satisfactory way for the protection of personnel resides in the use of canisters of the gas mask type such as are shown in Patent No. 1,537,519 to M. Yablick, as well as in various other patents. If the canister fill is not of this reagent it

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suffices to position a thin layer of the reagent against the canister window. In the presence of an alcohol the color change is visible through the canister window beginning at the inlet end of the canister and progressing toward the outlet end as the reagent is progressively reacted. Thus the position of the color front gives an immediate indication of the degree of exhaustion of the canister, and when the color change has occurred up toward the outlet it is evident that the discard point has been reached.

Alternatively, for spot checks the reagent may be disposed in a glass or other transparent tube of small diameter the ends of which are sealed as described in U.S. Patent 2,174,349 to John B. Littlefield. The reagent tube is used by breaking the seals and aspirating the atmosphere to be tested through it. Appearance of the color change indicates, of course, the presence of an alcohol.

Color standards for comparison with the color change may be provided in the manner known in this general testing field.

The hexavalent chromium compound may be supplied as chromium trioxide (CrO_3) or as a soluble chromate or dichromate, e.g., potassium (or other alkali metal) chromate (K_2CrO_4) or dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). The phosphoric acid may be orthophosphoric acid (H_3PO_4) or metaphosphoric acid (HPO_3) or other acid of pentavalent phosphorus.

The two constituents of the reagents may be used in such proportions as to provide per 100 ml. of silica gel about 0.022 gm. to 24 gms. of pentavalent phosphorus and about 0.0145 gm. to 2.6 gms. of hexavalent chromium.

The most vivid color change contrast is to be had by the use of about 0.05 gm. to 3 gms. of chromium trioxide and from about 0.15 gram to 9 gms. of metaphosphoric acid per 100 milliliters of silica gel, most suitably of 8 to 14 mesh size, with the preferred proportions being 0.53 gm. of chromium trioxide and 1.67 gms. of metaphosphoric acid.

The reagent may be prepared satisfactorily by addition of the reagents to about 16 milliliters of water and mixing the silica gel with the solution. When a relatively coarse silica gel is used, say of about 8 to 14 mesh, the introduction of water causes it to break down into particles finer than are desirable for the purposes of the invention. This may be avoided by using silica gel that has been humidified by exposure to humid air. The impregnated silica gel is then vacuum dried until it is free flowing, preferably to a water content of about 10 to 12 percent by weight.

The carrier, preferably a granular adsorbent, does not enter into the color-producing reaction but serves merely as an inert physical carrier for the reagent, thus avoiding the necessity for liquid reagents with their attendant disadvantages. Among the various carriers that might be used in HCl purified silica gel which, being colorless, insures maximum intensity of the color change.

The invention is applicable also to the quantitative determination of a wide variety of alcohols in air, and in many cases to determination of the Threshold Limit Value (T.L.V.) of the ACGIH, i.e., the concentration to which all workers may be exposed repeatedly day after day without adverse effect.

In the practice of the invention as described above the occurrence of the color change may be used to show the presence of an alcohol. Or, using a fixed volume of air at a fixed flow rate (supplied, for example, by a pump such as that described in U.S. Patent 3,166,938 to Weyrauch et al.) the length over which the color change occurs, as in the tubes referred to above, quantitative determination is possible by comparison with calibrated results. For example, using a pump such as described above delivering 100 ml. of air per stroke iso-amyl alcohol was

calibrated as follows. The tubes were 3.0 ± 1 mm. I.D. with a reagent bed depth of 50 mm. ± 5 mm. held in place by end plugs of fiber glass tape. They were first sealed at one end, dried at 250° C. overnight, filled and the other end sealed.

Iso-amyl alcohol in air-conc. (p.p.m.)	Stain length, 5 pump strokes (mm.)	Stain length, 10 pump strokes (mm.)
0	0	0
50	6	9
100 (T.L.V.)	8	12
200	10.5	17
300	13	21
400	15	25
500	17	29
600	20.5	36
800	22	40
1,000		

The length over which the stain is produced by a given alcohol will generally be greater as a result of passage of a larger volume of air, as indicated by the foregoing table, thus increasing the sensitivity and utility of the invention.

Other alcohols were similarly calibrated:

Compound	T.L.V. (p.p.m.)	Calibration (p.p.m.)
n-Amyl alcohol	N.L.	25-2,000
Iso-amyl alcohol	100	50-1,000
Sec-amyl alcohol	N.L.	25-2,000
Tert-amyl alcohol	N.L.	25-2,000
n-Butyl alcohol	100	50-4,000
Iso-butyl alcohol	N.L.	50-4,000
Sec-butyl alcohol	N.L.	50-4,000
Tert-butyl alcohol	100	100-800
Cyclohexanol (hexalin)	50	25-1,000
Ethyl alcohol	1,000	200-10,000
Ethylene glycol monobutyl ether (2-butoxy-ethanol) (butyl Cellosolve)	50	25-800
Ethylene glycol monoethyl ether (2-ethoxy-ethanol)	200	50-1,000
Furfuryl alcohol	50	25-500
Methyl alcohol	200	100-10,000
Methyl amyl alcohol (methyl isobutyl carbino)	25	25-1,00
2-methyl cyclohexanol	100	25-8000
Iso-propyl alcohol	400	100-10,000
Propyl alcohol	N.L.	100-10,000

N.L.—No threshold limit value listed in the ACGIH Threshold Limit Values Booklet for 1964.

The foregoing data illustrate the general applicability of the invention to alcohols, and to wide ranges of concentration in air. A few alcohols (benzyl alcohol, glycidol) produce very short stain lengths up to saturated vapor in air and therefore calibration is of little value although the occurrence of staining shows the presence of those alcohols. Diacetone alcohol is the only alcohol in air that has been found to produce only a trace of change up to 100 p.p.m. in air.

The reagents of the invention may not give fully accurate quantitative results below about 60° F. (stain length short); below that temperature acceptable results will be had at 40° to 60° F. if the tube is warmed in the hand while testing so that no correction factor will be necessary.

Changes in water vapor content of the air (20 to 80% RH) being tested do not interfere with the results. Likewise, such organic compounds as acetone, benzene and hexane do not interfere. And the results are acceptably independent at from 70° to 100° F. The stain may have a light end point when first formed but after about two minutes the stain intensity increases to give a clear end point. Tests have shown that when protected from the atmosphere the reagents of this invention may be expected to have a shelf life of about two years.

Although the invention has been described with particular reference to silica gel as the reagent carrier it will be understood that other substances may be used such as alumina, glass cloth, filter paper, and the like.

According to the provisions of the patent statutes, I have explained the principle of my invention and have described what I now consider to represent its best embodiment. However, I desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

I claim:

1. In a method of detecting an alcohol in air the step consisting of passing air, to be tested for the presence of alcohol, into contact with a reagent consisting essentially of a soluble hexavalent chromium compound and a pentavalent phosphoric acid supported by an inert carrier and providing from 0.0145 gram to 2.6 grams of hexavalent chromium and from 0.022 gram to 24 grams of pentavalent phosphorus per 100 ml. of silica gel, the reagent undergoing a color change in the presence of said alcohol.

2. A method according to claim 1, said reagent consisting essentially of chromium trioxide and metaphosphoric acid supported by silica gel in the proportions of about 0.15 gram to 3 grams of chromium trioxide and from about 0.15 to 9 grams of metaphosphoric acid.

3. A method according to claim 1, the reagent having a water content of about 10 to 12 percent by weight.

4. A method according to claim 2, the reagent consisting of chromium trioxide and metaphosphoric acid in the proportion of 0.53 gram of the former to 1.67 gram of the latter.

References Cited

UNITED STATES PATENTS

2,939,768 6/1960 Grosskopf ----- 23-232
3,223,488 12/1965 Luckey ----- 23-254

OTHER REFERENCES

50 Merck Index, seventh edn., p. 1003, 1960.

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