Oct, 3, 1972 T. HIRSCHFELD 3,695,847

HYDROCARBON DETECTOR

Filed Nov. 15, 1971 3 Sheets-Sheet 1

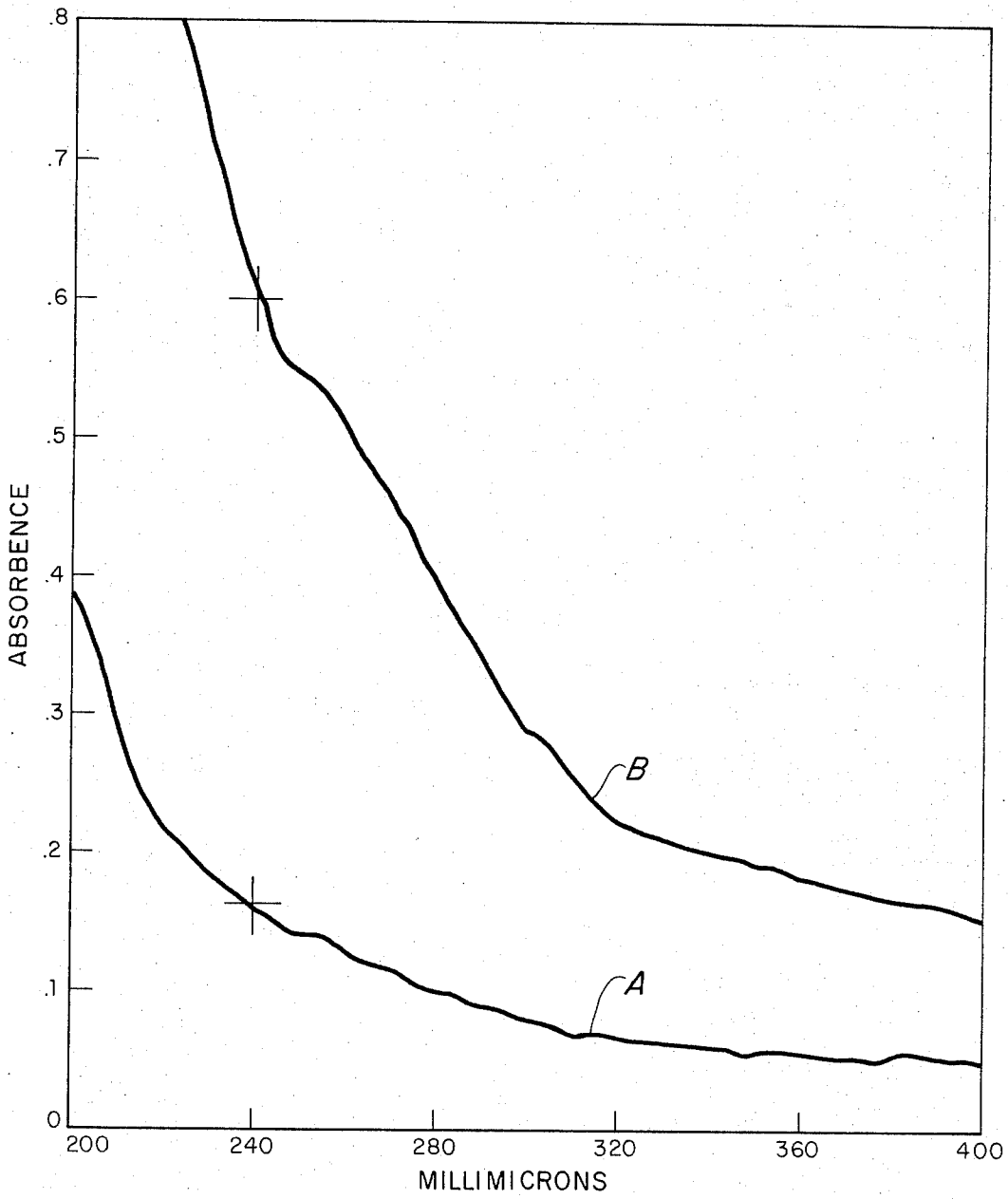


FIG. 1.

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HYDROCARBON DETECTOR

Filed Nov. 15, 1971 3 Sheets-Sheet 2

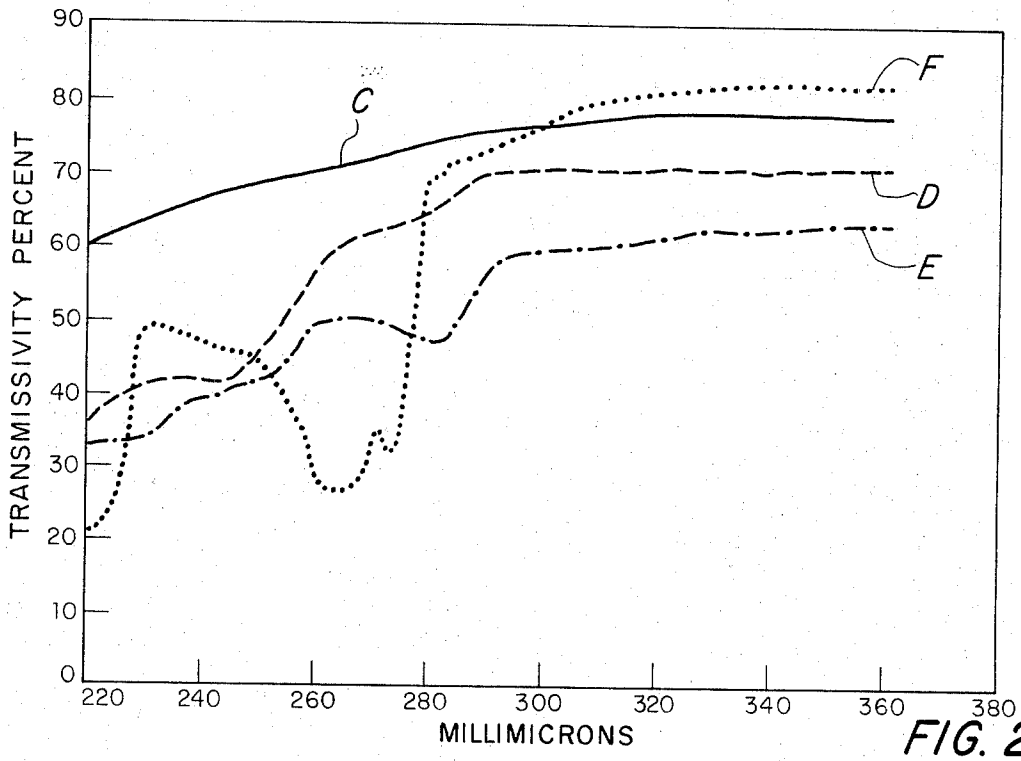


FIG. 2.

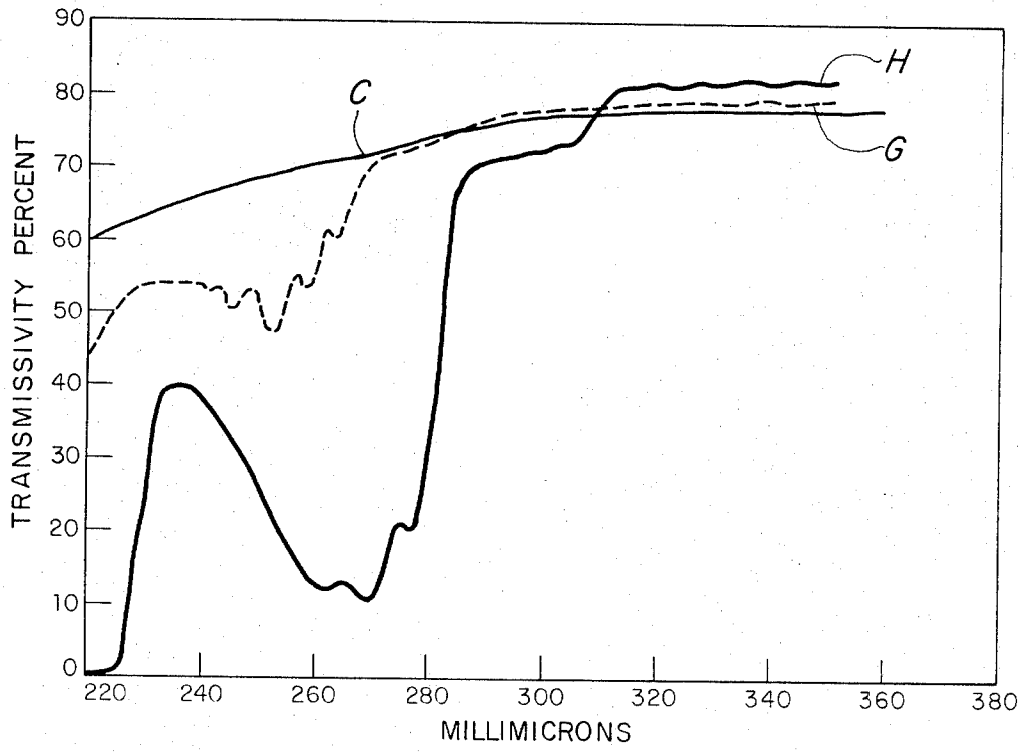


FIG. 3.

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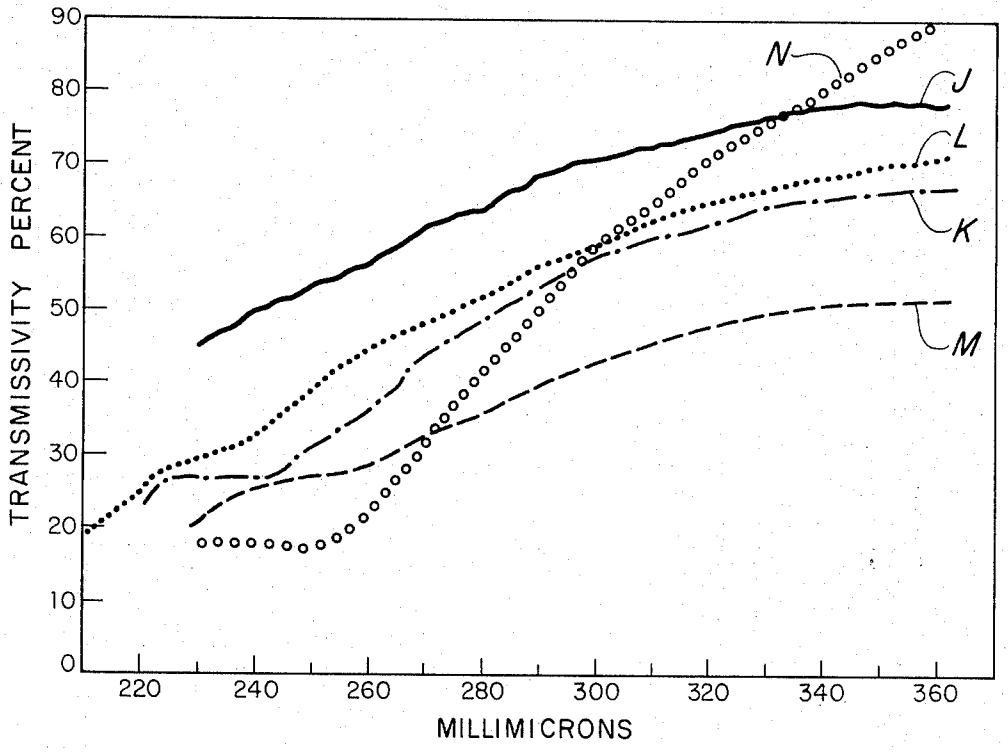


FIG. 4.

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United States Patent Office 3,695,847 Patented Oct. 3, 1972

3,695,847

HYDROCARBON DETECTOR

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Continuation-in-part of abandoned application Ser. No. 138,717, Apr. 29, 1971. This application Nov. 15, 1971, Ser. No. 198,982

Int. Cl. G01n 21/38, 33/22

U.S. Cl. 23—232 R 18 Claims

ABSTRACT OF THE DISCLOSURE

Method of detecting the vapors of aromatic and unsaturated hydrocarbon by reacting the vapor with a film of polytetrafluorethylene sulfonic acid, and examining the ultraviolet transmission characteristics of the reacted film.

This application is a continuation-in-part of copending application Ser. 138,717, now abandoned, filed Apr. 29, 1971.

This invention relates to the detection and measurement of hydrocarbon vapors, and more particularly to the detection and measurement of unsaturated and aromatic hydrocarbons.

The term "vapor" as used herein is intended to include hydrocarbons in gaseous form as well as liquid-gas aerosols in which the hydrocarbon forms either or both phases.

The term "hydrocarbon" as used herein is intended to include compounds which consist solely of carbon and hydrogen, and such compounds which are incompletely substituted, at least to the extent that more C—H moieties or parts remain in the molecule.

It is known that atmospheric pollutants include a large number of materials having a hydrocarbon structure, particularly the pyrolytic products of partially burned gasoline and residual unburned gasoline. The major components of such products of incomplete burning in internal combustion engines are largely vaporous unsaturated and aromatic hydrocarbons.

The detection and measurement of such vaporous hydrocarbons has heretofore been a difficult and cumbersome task. The use of infra-red absorption spectroscopic techniques directly on automobile exhaust gases has been unsatisfactory primarily because the high water vapor content of the exhaust gases makes the latter infra-red opaque in many wide spectral bands. The use of gas chromatography is slow and very expensive, and flame ionization techniques are also very expensive, not adequately selective and the equipment is very delicate.

A principal object of the present invention is to provide an improved and novel method of and means for the detection of unsaturated and aromatic hydrocarbon vapors quickly and economically.

Yet other objects of the present invention are to provide such a detection system which requires little formal training to use, and to provide such a system in which the necessary equipment can be simple and inexpensive.

To effect the foregoing and other objects of the present invention, generally one employs as a detector a material which is reactive with unsaturated or aromatic hydrocarbons, exhibits diffusivity to the vapors of such hydrocarbons, forms different compounds each with a corresponding unique physical characteristic upon reaction with specific ones of such hydrocarbons, and contains no hydrocarbons itself. Where the detection of the compounds formed upon reaction with hydrocarbons is accomplished optically, it is preferred that the material has a high transmissivity at the wavelength pass band of the detecting radiation. Where one wishes to use the material in a high temperature environment, it is preferred that the material be a completely fluorinated polymer.

Other objects of the invention will in part be obvious and will in part appear hereinafter. The invention accordingly comprises the method involving the several steps and the relation of one or more of such steps with respect to each of the others as exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the present invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

FIG. 1 is a plot of wavelengths against absorbence showing the comparison between unreacted polymer and polymer reacted in accordance with the present invention with hydrocarbon vapors present in an automotive engine exhaust;

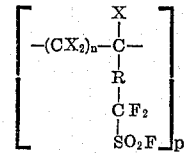
FIG. 2 is a plot of wavelengths against transmissivity showing the characteristics of the reaction product of different aromatics with the polymer according to the present invention;

FIG. 3 is a plot similar to FIG. 2 showing reaction product characteristics of yet other aromatics; and

FIG. 4 is a plot similar to FIG. 2 showing reaction product characteristics of different unsaturates with the polymer according to the present invention.

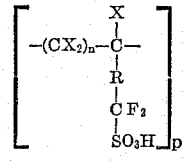
In a preferred form of the invention, the material employed for hydrocarbon detection is a polymeric material which is a homogeneous film of a completely halogenated alkene based polymer containing pendant sulfonyl groups. The film is manufactured as a fluorosulfonyl derivative having a generalized formula

(1)



where X is a halogen, n and p are integers, and R is a moiety selected from the groups $(—O—(CF_2)_m—)$, $(—R'—(CF_2)_m—)$ and $(—(CF_2)_m—)$ wherein the terminal $—CF_2—$ radical of those groups is bonded to the CF_2 radical connected to the sulfonyl group, m is an integer from 1 to 6, R' is a perhalogenated alkyl biradical having from 1 to 6 carbon atoms. This material is usually hydrolyzed to the sulfonic acid form described as

(2)



The two compounds described above (1) and (2) are highly reactive and react with appropriate unsaturated or aromatic hydrocarbons covalently.

Both of the compounds or derivatives are structures of a completely halogenated polymer that essentially has a polyperhaloalkene based type of backbone with sulfonyl derivative (i.e. $—SO_2—$) ended side chains and substantially lacks any hydrocarbon groups. The presence of O or R' in the molecule does not materially affect the reactivity or use of the material for purposes of the invention, nor if $m>1$ is the reactivity materially affected. The molecular weight of the material is not particularly important inasmuch as the desired reactivity with the particular hydrocarbon gases is due to the presence

of the fluorsulfonyl groups. In this regard, the number of sulfonyl groups can be varied as can the number of CF_2 groups. The halogen substitutions on the backbone can be either fluorine, chlorine or other halogens in mixed porportions, but the backbone should be perhalogenated to insure that substantially no hydrogens remain bonded to the molecule. Typically then, the molecular backbone if perfluorinated, is similar to the polytetrafluorethylene type of backbone; and if partially chlorinated then similar to the backbone of Kel-F (a trademark of the 3M Company) i.e. a chloro 3-fluorethylene polymer with fluorsulfonyl side chains. Thus, the polymeric material can vary fairly widely in molecular weight, retention capacity, and electrical and mechanical characteristics. However, where the polymer is preferably substantially completely halogenated and possess reactive fluorsulfonyl side chains, it will provide the properties required for purposes of the invention. Generally, it is preferred to use polymers of the lowest equivalent weight provided that the weight is not so low that the polymer becomes unstable at room temperature. This serves to increase the ratio of sulfonyl groups to carbon atoms and thus increase the retention capacity.

Polymers of this type are described more fully in U.S. Pat. No. 3,282,875, and an exemplary film thereof if available from E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. under the trade designation "XR Perfluor-Sulfonic Acid Membranes."

As is characteristic of this type of polymeric structure (herein caller perhaloalkene sulfonyl polymers), hydrocarbon vapors, both unsaturates and aromatics, tend to diffuse readily into the polymer. The polymeric material has an upper use temperature, typically around 225° C. for the above-identified film depending on the equivalent weight of the membrane (usually up to about 1300 equivalent weight range), the environment employed and the desired service life.

It has now been found that this perfluoralkene sulfonyl material such as polytetrafluorethylene sulfonic acid will readily react with the vapor of certain hydrocarbons which contain one or more multiple carbon to carbon bond, and one or more CH_m moiety (where m is an integer from 1 to 3), which hydrocarbons may be typified generally as the aromatic hydrocarbons and the unsaturated hydrocarbons. Obviously, the ambient temperature and pressure, as well as the nature of the hydrocarbon determines if the vapor pressure of the latter is sufficient to provide sufficient hydrocarbon to establish a detectable reaction. Typically, the perfluorosulfonic acid type membrane will react with the vapors of such aromatics as benzene, xylene, anthracene, naphthalene carbazole and even mixtures such as ligroin or petroleum ether. The membrane will also react with the vapors of unsaturates such as alkenes, conjugated dienes, alkynes, and the like. Additionally, the material substantially does not react with saturated hydrocarbons or alkanes such as methane and the like.

The reaction with hydrocarbon vapors is believed due to a sulfonation reaction in which the hydrocarbon vapor molecules R'' is attached at the perfluorosulfonyl —$CF_2 \cdot SO_2$— sites to form a sulfone derivative wherein the terminal group then becomes (—$CF_2 \cdot SO_2R''$).

Each derivative, depending on the nature of the reacting vapor molecule, possesses unique physical characteristics which can be detected readily. For example, the derivatives formed by reacting the membranes with vapors of hydrocarbons have strong characteristics absorptions in the ultraviolet, which shift toward the visible for polynuclear aromatic hydrocarbons. Because the transmissivity of the prefluorosulfonic acid type membrane includes a wavelength pass band well into the ultraviolet, one may examine the reacted film for ultraviolet absorption characteristics.

Thus, in one form of the invention, a film of perfluorethyelne sulfonyl membrane is exposed to the vapors

of a hydrocarbon having one or more multiple carbon-to-carbon bonds, causing the hydrocarbon to exchange at the sulfonyl end sites and form a derivative compound. The extent of the reaction is highly dependent on the concentration of the reacting hydrocarbons in the vapor and the length of time that the membrane is exposed to the hydrocarbon vapor. Thus, the detector, in effect, time integrates the hydrocarbon concentration, and the density of the product or derivative formed can be a measure of concentration. The membrane should be protected, as by gas or vapor impervious packaging, prior to use.

If now, for example, one opens a package containing the membrane and places the latter in the exhaust stream of an automobile for a short period such as five minutes, sufficient reaction should have occurred to detect any significant level of the detectable hydrocarbons. One can now examine the reacted membrane in a number of ways.

For example, the reacted membrane can be exposed to a radiation source such as a quartz-mercury lamp which typically has a high emission peak at about 254 mμ. The lamp, if desired, can be filtered at a passband with a known UV filter centered on the above wavelength. One can prepare a standard such as a calibrated gray scale or density step scale for that passband on the basis of exposing samples of the membrane for identical periods to various concentrations of known automobile exhaust products. By then, matching the percentage absorption of the radiation passed through the gray scale with the percentage absorption of the radiation passed through the membrane reacted with the exhaust gases under test, one can readily detect the presence of and obtain a quantitative measure of the hydrocarbon content per cubic meter of exhaust, at least with respect to those hydrocarbons that react with the membrane to provide derivative compounds having significant absorption in the selected passband.

Alternatively, of course, one need merely examine the transmission characteristics of the reacted membrane by sweeping a radiation source through a range of wavelengths and transmitting the radiation through the membrane. Typically, this is accomplished in a UV spectrophotometer. The intensity of the radiation transmitted for each wavelength produces a characteristic UV absorption curve which can be correlated with the hydrocarbon with which the membrane reacted. Such spectral curves and the method of obtaining same in UV, infrared and visible passbands is well known in the art.

The method of the invention was carried out with a number of different appropriate hydrocarbons as follows:

The material used was the XR Perfluorosulfonic acid type membrane obtained from E. I. du Pont de Nemours. The membrane was first exposed for a few minutes to steam which was found to clear the membrane of any hydrocarbon derivatives and to return the membrane to a hydrolyzed condition. The membrane can be cleansed in this manner and, if desired, used repeatedly.

The cleansed membrane was then examined in a scanning UV spectrophotometer to determine its own transmission characteristics. A typical wave of the membrane material as shown in FIG. 1 is the transmission curve A between about 200 to 400 mμ plotted against an ordinate of fractional absorption. Thus, for example at 240 mμ, the absorbence is about 0.17. The membrane was then exposed for about five minutes directly in the exhaust stream from an idling internal combustion gasoline engine and then examined again in the spectrophotometer. The curve in FIG. 1 marked B is the result. Of interest is that at the 240 mμ abscissa, the absorbence has changed to about .6, i.e., by a factor of more than 3, and the absorbence over the entire range has increased markedly over curve A.

That the foregoing is due to the presence of hydrocarbons of unsaturated and/or aromatic nature is evidenced by a number of other experiments in which cleaned

samples of the membrane were exposed for about one minute each to various vapors at about room temperature. As shown in FIGS. 2 and 3, there is plotted the transmission percentage against wavelength for a number of samples of the perfluorosulfonic acid membranes exposed to a corresponding number of vapors of aromatic compounds. The curve C in both FIGS. 2 and 3 is the plot for the steam-cleansed membrane. The various curves are identified according to the reactant vapor as follows:

Curve D—anthracene
Curve E—carbazole
Curve F—xylene
Curve G—petroleum ether
Curve H—naphthalene

Even allowing for experimental error, the amplitude and shapes of curves D to H inclusive are quite distinctive and differ considerably from the transmission curve for the unexposed material, particularly around the band between 220 to 280 mμ.

In FIG. 4, there is shown a plot of wavelength vs. transmission percentage for a number of samples of unsaturates and a compound which has both mixed aromatic and unsaturated portions. The curve J is for the basic steam-cleansed membrane of the thickness used for these examples. The various curves are identified as follows by the reactant vapor:

Curve K—cyclohexene
Curve L— isoprene
Curve M—α-pinene
Curve N—α-methylstyrene

The latter of these curves (N) is amplified by a factor of 10 with respect to transmissivity.

If in place of the sulfonic acid form of the copolymer, one employs the sulfonyl fluoride form, the experimental results will be substantially the same.

Since certain changes may be made in the above method without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted in an illustrative and not in a limiting sense.

What is claimed is:

1. Method of detecting the vapor of a hydrocarbon having multiple carbon to carbon bonds and comprising the steps of

exposing a perfluoroalkene sulfonyl polymer to said vapor for a sufficient time and in sufficient concentration to alter a physical characteristic of said polymer by reacting said vapor with the sulfonyl end groups on said polymer, and

detecting the presence of said altered physical characteristic.

2. Method as defined in claim 1 wherein said polymer is polytetrafluorethylene sulfonic acid.

3. Method as defined in claim 1 wherein said polytetrafluorethylene is sulfonyl fluoride.

4. Method as defined in claim 1 wherein said physical characteristic is the ultraviolet absorption of said polymer.

5. Method as defined in claim 4 wherein said polymer is in sheet form, and wherein said detecting step comprises exposing the reacted polymer sheet to a source of ultraviolet radiation and measuring the comparative absorption-transmission characteristics of said reacted sheet with respect to unreacted polymer sheet for said radiation.

6. Method as defined in claim 5 wherein said characteristics are measured substantially over a narrow wavelength band.

7. Method as defined in claim 5 wherein said radiation includes wavelengths at least in the 220 to 280 mμ region.

8. Method as defined in claim 7 wherein said characteristics are measured substantially over said entire region.

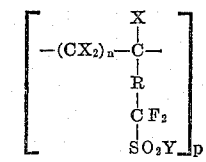
9. Method as defined in claim 8 wherein said radiation comprises a band covering at least about the 240 to 260 mμ wavelength region.

10. Method as defined in claim 9 wherein said radiation is in a band including an emission peak at about 254 mμ.

11. Method of detecting the vapor of a hydrocarbon having multiple carbon to carbon bonds and comprising the steps of

exposing a polymer to said vapor for a sufficient time and in sufficient concentration to alter a physical characteristic of said polymer by reacting said vapor with sulfonyl end groups on said polymer, and

detecting the presence of said altered physical characteristic, said polymer having the generalized formula



where X is a halogen, n and p are integers, and R is a moiety selected from the group consisting of the radicals [—O—$(CF_2)_m$—],

[—R'—$(CF_2)_m$—]

and [—$(CF_2)_m$—] wherein the terminal —CF_2— portion of said radicals is bonded to the CF_2 portion connected to the sulfonyl group, m is an integer, R' is a perhalogenated alkyl biradical having from 1 to 6 carbon atoms, and Y is selected from the group consisting of F and OH.

12. Method as defined in claim 11 wherein said physical characteristic is the ultraviolet absorption of said polymer.

13. Method as defined in claim 12 wherein said polymer is in sheet form, and wherein said detecting step comprises exposing the reacted polymer sheet to a source of ultraviolet radiation and measuring the comparative absorption-transmission characteristics of said reacted sheet with respect to unreacted polymer sheet for said radiation.

14. Method as defined in claim 13 wherein said characteristics are measured substantially over a narrow wavelength band.

15. Method as defined in claim 13 wherein said radiation includes wavelengths at least in the 220 to 280 mμ region.

16. Method as defined in claim 15 wherein said characteristics are measured substantially over said entire region.

17. Method of detecting in the exhaust fumes of internal combustion engines the presence of the vapors of hydrocarbons having multiple carbon to carbon bonds, and comprising the steps of

exposing a film of perfluoralkene sulfonyl polymer to said fumes for a sufficient time and in sufficient concentration to react polymer with said vapors, and

determining the extent of change of transmission of said film to ultraviolet radiation.

18. Method as defined in claim 17 wherein said polymer is polytetrafluorethylene sulfonic acid.

References Cited

UNITED STATES PATENTS

3,282,875	11/1966	Connolly et al.	260—29.6 F
3,560,159	2/1971	Goetz	23—232 R
3,102,192	8/1963	Skala	23—232 R
2,490,345	12/1949	Flatford et al.	23—232 R

MORRIS O. WOLK, Primary Examiner

E. A. KATZ, Assistant Examiner

U.S. Cl. X.R.

23—230 HC, 254 R; 250—71 R

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,695,847 Dated October 3, 1972

Inventor(s) Tomas Hirschfeld

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 57, the words -- polymer is-- should be inserted before "polytetra-"

Column 5, line 58, the word "is" should be cancelled.

Signed and sealed this 22nd day of May 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
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