A colorimetric device for indicating carbon dioxide is disclosed, which device contains: a) at least one pH-sensitive indicator dye, b) at least one basic substance selected from the group consisting of quaternary ammonium salts, phosphonium salts and sulphonium salts, and c) at least one member selected from the group consisting of water-insoluble, organic substances of low volatility, which are not susceptible to alkaline hydrolysis and are liquid at room temperature or moderately elevated temperatures.
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A COLORIMETRIC DEVICE FOR INDICATING CARBON DIOXIDE

Technical field
The present invention relates to a colorimetric device for indicating carbon dioxide.

Technical background
Methods for the detecting or measuring the concentration of gaseous carbon dioxide (CO₂) in a mixture of gases utilizing chemical absorption belongs to the well-known technique.

German Patents Nos 919510 and 1 007 525 both discloses selective absorption of CO₂ on a substance which contains a pH-sensitive dye. The change in the pH-value caused by the CO₂ bound to the substance becomes apparent as a change in colour of the dye which is present in the substance. Accordingly the change in colour becomes a measure of the content of CO₂ in the gas flow under investigation.

The problems encountered with these early systems are that the absorbing surface must be kept in hermetically closed glass tubes and that, once said surface gets into contact with the gas flow, an irreversible reaction is obtained, i.e. the device becomes unusable after having been exposed to the test gas. Thus it cannot be used e.g. for monitoring CO₂ concentrations which vary with time.

A reversible CO₂ indicator device is disclosed in US-A-4 278 499. This prior art device comprises a system consisting of a pH-sensitive indicator dye, a basic substance and a viscous hygroscopic liquid. The indicator is able both to absorb and desorb CO₂ with a time constant of a few seconds so that it can be used e.g. in hospitals for monitoring the breathing of a patient. During exhalation, which takes about 4 seconds, the air contains 3-5 % by volume of CO₂ whereas the CO₂ content during inhalation, which typically takes
about 2 seconds, is about 0.05% by volume corresponding to the normal concentration of \( \text{CO}_2 \) in atmospheric air. The indicator hence changes colour to and fro with breathing about 10 times a minute.

The main disadvantage of this known system is that it is strongly hygroscopic and hence the indicator will absorb water vapour from the gas under investigation ultimately resulting in that the system ceases to respond to \( \text{CO}_2 \).

In view of the fact that exhaled air is saturated with water vapour at about 30°C this indicator will only be able to monitor the breathing of a patient for a few minutes.

Another disadvantage exhibited by this prior art device is that the indicator must be stored in a hermetically closed, absolutely dry environment free from carbon dioxide prior to use.


These systems are based on pH-sensitive indicator dyes, water-insoluble organic quarternary (e.g. ammonium or phosphonium) hydroxides as a basic substance and additional substances in order to facilitate the absorption/desorption of \( \text{CO}_2 \).

These known indicator devices appear to function reversibly for several days and they are indicating satisfactory both in humid and dry environments.

The major disadvantage of these devices is that the strong base decomposes with time so that the indicator slowly becomes permanently "acid" and accordingly useless. Then it exhibits the "acid" colour all the time as if it were exposed to a constantly high concentration of \( \text{CO}_2 \).
Also, in the presence of moisture traces, alkaline hydrolysis of phosphate esters etc used as plasticizers produces acidic materials that consume the strong base.

This decomposition of the base is strongly depending on the temperature of the environment and hence the useful length of life on an indicator device which has been stored while awaiting use is difficult to predict and check.

It is an object of the present invention to provide a reversible colorimetric device for indicating carbon dioxide which does not need to be stored in a hermetically closed, absolutely dry environment free from carbon dioxide prior to use.

It is another object of the present invention to provide a reversible colorimetric device for indicating carbon dioxide with increased shelf life to comply with the requirements which should be put on a mass-produced product, e.g. for use in medical service.

The invention

The present invention provides a colorimetric device for indicating carbon dioxide which device contains

a) at least one pH-sensitive indicator dye,

b) at least one basic substance selected from the group consisting of quaternary ammonium salts, phosphonium salts and sulphonium salts, and

c) at least one member selected from the group consisting of water-insoluble, organic substances of low volatility, which are not susceptible to alkaline hydrolysis and are liquid at a temperature preferably below 100°C.

According to a preferred embodiment of the colorimetric device according to the invention said device also contains

d) an inert, porous gas permeable carrier for components a) to c).
This component d) can be any conventional carrier used in connection with the conventional colorimetric devices such as a paper sheet but is preferably a thin cellulose layer applied on a transparent thin plastics foil, in which latter case observation of the device from both sides is enabled.

According to the invention the pH-sensitive indicator dye to be used in the device according to the invention can be any dye which has been used in the prior art, reversible colorimetric devices discussed above such as thymol blue, m-cresol purple and cresol red.

Substances to be used as component b) in the colorimetric device according to the invention can be summarized by the general formula (I):

\[
R^2 \\
R^1 - X^+ - R^3 - Y^- \\
R^4
\]  

(I)

wherein

X represents N, P or S;
R^1, R^2, R^3 and R^4, which may be equal or different, each represents (C_1 - C_{20}) alkyl; (C_1 - C_{4}) alkyl which is substituted with a (C_1 - C_{4}) alkyl or a phenyl group; naphthyl; benzyl; or pyridyl;

Y^- is an anion selected from the group consisting of hydroxide, fluoride, chloride, bromide, iodide, carbonate and tetrafluoroborate.

Another example of substances which can be used as component b) in the colorimetric device according to the invention are pyridinium compounds of the general formula (II):

\[
\text{N}^+ - R^5 - Y^- \]  

(II)

wherein
$R^5$ is selected from the group consisting of (C$_1$ - C$_{20}$) alkyl and benzyl and
$Y^-$ is an anion selected from the group consisting of hydroxide, fluoride, chloride, bromide, iodide, carbonate and tetrafluoroborate.

Still another example of substances which can be used as component b) in the colorimetric device according to the invention are imidazolinium compounds of the general formula (III)

\[
\begin{array}{c}
\text{H}_2\text{C} - \text{N} \\
\text{R}^6 \\
\text{C} - \text{R}^8 \\
\text{H}_2\text{C} - \text{N}
\end{array}
\]

wherein
$R^6$ represents (C$_1$ - C$_{20}$) alkyl,
$R^7$ represents (C$_1$ - C$_{20}$) alkyl, which is optionally substituted with hydroxyl or amino groups, and
$R^8$ represents H or (C$_1$ - C$_{50}$) alkyl, which is linear or branched, saturated or unsaturated or contains ring structures.

Component c) of the colorimetric device according to the present invention is at least one member selected from the group consisting of water-insoluble, organic substances of low volatility, which are not susceptible to alkaline hydrolysis and are liquid at room temperature or moderately elevated temperatures, preferably below 100°C.

Besides being non-toxic, component c) should also preferably be non-irritating in the concentrations used in the colorimetric device according to the invention.

The term "not susceptible to alkaline hydrolysis" is meant here and in the claims to exclude i.a. compounds containing
ester groups which are subjected to alkaline hydrolysis in the presence of the basic component b).

Component c) is most preferably one or more substances which is liquid at room temperature (about 25°C), or is semi-solid, e.g. of waxy structure, at room temperature but becomes liquid at moderately elevated temperatures, preferably below 100°C.

According to one aspect of the present invention, component c) will be one or more substances having a molecular weight (weight average molecular weight = $M_w$) below 15000, preferably below 10000.

According to another aspect of the present invention, component c) is at least one member of the group consisting of alcohols, phenols and alkoxyalted derivatives of such substances, advantageously at least one linear or branched polyether.

Accordingly to a preferred embodiment of this aspect of the invention component c) comprises at least one compound having one of the following structures:

\[
\begin{align*}
\text{(IV)} & \quad R^9-(O-R^{10})_m-(O-R^{11})_n-O-R^{12} \\
\text{(V)} & \quad R^9-(\text{CH}_2)_m-(O-R^{11})_n-O-R^{12} \\
\text{(VI)} & \quad R^9-S-R^{13}-(O-R^{10})_m-(O-R^{11})_n-O-R^{12} \\
\text{(VII)} & \quad (R^9)_{q-N}(R^{13}-(O-R^{10})_m-(O-R^{11})_n-O-R^{12})_r
\end{align*}
\]

wherein $R^9$ and $R^{12}$ each represents H or a linear or branched hydrocarbon residue of 1 to 50 carbon atoms, optionally containing one or more double bonds, triple bonds and/or ring structures, $R^{10}$, $R^{11}$ and $R^{13}$ each represents a linear or branched hydrocarbon residue of 1 to 10 carbon atoms.

$m$ and $n$ are equal or different integers from 0 to 100,
p is an integer from 1 to 6, and
q and r are equal or different integers from 0 to 4.

Examples of compounds having the above structures (IV) to (VII) are the following:

Polyalkylene glycols, such as polymethylene glycols, polyethylene glycols, polypropylene glycols, polybutylene glycols and copolymers of ethylene oxide, propylene oxide and/or butylene oxide.

Other linear polyethers, such as polytetrahydrofurans.

Alkoxylated alcohols or phenols, such as ethoxylated, propoxylated or butoxylated alcohols derived from fatty alcohols (straight or branched, saturated or unsaturated, etc), alkyl phenols, dialkyl phenols, alkyl naphthalenes, bisphenol A, alkyne diols, lanolin, cholesterol, phytosterol, sitosterol, glucose ethers and silicones; and mixed ethoxylated/propoxylated alcohols.

Branched polyethers, for instance products obtained by ethoxylating and/or propoxylating trimethylol propane or pentaerythritol.

Alkoxylated amines, such as ethoxylated and/or propoxylated primary or secondary amines or diamines.

Alkoxylated (ethoxylated and/or propoxylated) thiols.

Dialkyl ethers, e.g. dioctyl ether.

The colorimetric device according to the invention is prepared in a conventional way by mixing components a), b) and c) in a volatile organic solvent, such as a lower aliphatic alcohol, e.g. methanol, and applying the solution on a
carrier, e.g. a paper sheet, whereafter the solvent is evaporated.

The enclosed drawing (Figure 1) shows a comparison between a prior art colorimetric device (A) and a colorimetric device according to the invention (B) as to the shelf life in air at a constant relative humidity of 50% by volume.

The composition of the prior art colorimetric device (A) was: tetraoctylammonium hydroxide as the base, thymol blue as the pH-sensitive dye and 70% by weight (calculated on the total weight of the mixture) of tributyl phosphate as a further component.

The colorimetric device according to the invention (B) differed in composition from the one according to the prior art only in that the tributyl phosphate was replaced by the same amount of an alkyl aryl polyether alcohol having the formula

\[ C_{8}H_{17}-(OC_{2}H_{4})_{10}-OH \]

(Triton® X-100 from Rohm and Haas Nordiska AB, Stockholm, Sweden).

Figure 1 shows the shelf life (in logarithmic scale) as a function of temperature for the two devices.

The shelf life was defined as the time required for the indicator (without being in contact with \( \text{CO}_{2} \)) to become aged to such an extent that the "basic" colour is changed in the direction to the "acid" colour corresponding to an exposure to about 1% by volume of \( \text{CO}_{2} \).

From Figure 1 it is evident that the shelf life at 25°C was increased from about 16 days for the prior art device (A) to more than 30 months for the device according to the invention (B).
CLAIMS

1. A colorimetric device for indicating carbon dioxide, which device contains
   a) at least one pH-sensitive indicator dye,
   b) at least one basic substance selected from the group consisting of
      quaternary ammonium salts, phosphonium salts and sulphonium salts, and
   c) at least one member selected from the group consisting of
      water-insoluble organic substances of low volatility, which are not
      susceptible to alkaline hydrolysis and are liquid at room temperature or
      moderately elevated temperatures, preferably below 100°C.

2. A colorimetric device according to Claim 1, which also contains
   d) an inert, porous, gas permeable carrier for components a) to c), preferably a thin
      cellulose layer applied on a thin plastics foil.

3. A colorimetric device according to any of claims 1 and 2, wherein the organic
   substance(s) c) has/have a molecular weight (M_w) below 15000, preferably below 10000.

4. A colorimetric device according to any of claims 1 to 3, wherein component c) is
   at least one member of the group consisting of alcohols, phenols and alkoxylated
   derivatives of such substances.

5. A colorimetric device according to any of claims 1 to 4, wherein component c) comprises at least one linear or
   branched polyether.

6. A colorimetric device according to any of claims 1 to 5, wherein component c) comprises at least one compound having
   one of the following structures:
\[ R^9 - (O-R^{10})_m - (O-R^{11})_n - O-R^{12} \]  
(IV)

\[ R^9 - (CH_2 - (O-R^{10})_m - (O-R^{11})_n - O-R^{12})_p \]  
(V)

\[ R^9 - S - R^{13} - (O-R^{10})_m - (O-R^{11})_n - O-R^{12} \]  
(VI)

\[ (R^9)_q - N(R^{13} - (OR^{10})_m - (O-R^{11})_n - O-R^{13})_r \]  
(VII)

wherein \( R^9 \) and \( R^{12} \) each represents \( H \) or a linear or branched hydrocarbon residue of 1 to 50 carbon atoms, optionally containing one or more double bonds, triple bonds and/or ring structures,

\( R^{10}, R^{11} \) and \( R^{13} \) each represents a linear or branched hydrocarbon residue of 1 to 10 carbon atoms,

\( m \) and \( n \) are equal or different integers from 0 to 100,

\( p \) is an integer from 1 to 6, and

\( q \) and \( r \) are equal or different integers from 0 to 4.
INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 95/01363

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: G01N 31/22
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, ANALYTICAL ABSTRACTS, CA SEARCH, MEDLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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* Special categories of cited documents:
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Date of the actual completion of the international search: 26 April 1996

Date of mailing of the international search report: 02-05-1996

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