

## STATIONARY PHASES FOR GAS CHROMATOGRAPHY

### Field of the Invention

- 5 The present invention relates to stationary phases for use in gas chromatography columns, to chromatography columns containing the stationary phases, and to analytical and separation processes using the stationary phases.

### 10 Background of the Invention

Chromatography is a technique that is widely used for the analysis, partitioning and/or separation of compounds contained in a mixture of compounds. Gas chromatography is a form of chromatography that is used particularly for the  
15 analysis or separation of relatively volatile liquids or gases. For example, gas chromatography is used extensively in the petroleum industry for the separation of petroleum distillates into their constituent compounds in order to analyse the composition of the distillate.

20 Briefly, gas chromatography involves the separation (or partial separation) of compounds present in a gas stream using a gas chromatography column that contains a stationary phase (also known as a 'packing material' or an 'adsorbent'). The process of differential adsorption or interaction between the compounds and the stationary phase leads to the separation of the compounds  
25 from the mixture.

In use, a volatalised mixture of compounds is carried through the chromatography column by a carrier stream of inert gas. Interactions between the compounds and the stationary phase leads to separation of at least some of  
30 the compounds and these are then detected as they exit the column by a detector that is in fluid communication with the outlet of the column.

Stationary phases can take many forms, but for the purposes of description of the present invention, they essentially consist of a support material that is

evenly coated with a thin layer of a coating material in the form of a liquid phase. In a so-called 'packed column' the support material comprises a particulate solid of relatively uniform particle size. The particles fill a tubular column that is fabricated from stainless steel, glass, copper or other suitable material. In an alternative form, the column may be a 'capillary column' comprising a length of small bore tubing containing a thin layer of the coating material on the inside wall of the tube.

The composition of the stationary phase, and in particular, the coating material, determines at least in part the types of compounds that can be separated, as well as the degree of separation that can be achieved. Examples of stationary phases that are in use include OV-1 or SE-30 in the drug analysis field, and Chromosorb 102, Apiezon L, Dexsil, or OV-101 in the hydrocarbon field. The selection of a stationary phase for a particular application will depend at least in part upon the structure, polarity and the volatility of the compounds to be analysed.

In the field of petroleum analysis in particular, the demands on the stationary phase are very high as analysts strive to separate mixtures containing a number of structurally related or isomeric compounds that have similar molecular weight, polarity and/or volatility. An example in this field is the separation of isomers of butane.

Unfortunately, the capacity of many existing stationary phases to separate compounds of interest is not as great as would be liked. To improve separations using existing stationary phases it has become practice to join two or more columns in sequence to achieve sufficient separation of compounds. Clearly, there is a need for stationary phases that provide improved separations of compounds of interest.

Accordingly, the present invention aims to provide a packed column stationary phase that is able to separate one or more compounds from a mixture of compounds more efficiently than some of the existing stationary phases.

### Summary of the Invention

5 The present invention arises out of the inventor's research into alternative stationary phases that are particularly suitable for separations in the petroleum industry. In particular, the present invention arises out of the inventor's discovery that the resinous products from a condensation reaction between phenol-derivatives and aldehydes have a greater capacity to separate some  
10 mixtures of compounds than do some of the existing stationary phases.

Thus, the present invention provides a stationary phase for a gas chromatography column, the stationary phase including a support material and a coating material that is coated onto the support material, the coating material  
15 including a resinous product of a condensation reaction between one or more phenol-derivatives and one or more aldehydes.

When the stationary phase of the present invention is used in a gas  
20 chromatography column under standard conditions, the column is able to separate a liquified natural gas ('LNG') sample into its constituent C1-C34 aliphatic and aromatic compound mixtures in a single run on one column. To the best of the inventor's knowledge, this type of separation was previously only achieved with existing stationary phases by using a number of columns  
25 connected in series.

It will be appreciated that condensation reactions between phenol-derivatives and aldehydes can potentially produce a number of products depending upon the reaction conditions. For example, base catalysed reactions typically  
30 produce resinous type materials that are a product of condensation between the phenol and aldehyde groups. During the course of their studies, the inventors have developed a procedure for producing resinous phenol-derivative aldehyde condensation products and coating these onto a solid support. In a preferred form of the invention the resinous coating material is reacted with the solid

support to form covalent bonds between the coating material and the solid support.

Accordingly, the present invention also provides a process for preparing a stationary phase packing material for a gas chromatography column, the process including the steps of:

- (a) reacting one or more phenol-derivatives and one or more aldehydes in a condensation reaction in the presence of a catalyst to form a resinous coating material; and
- (b) coating a support material with the resinous coating material from step (a) to produce said stationary phase.

The present invention further provides a packed column for gas chromatography, the column containing a stationary phase of the type mentioned above.

As discussed, the inventor has found that the stationary phase of the present invention provides improved separations of some mixtures of compounds. Accordingly, the present invention also provides a process for separating one or more compounds from a mixture of compounds, the process including the steps of:

- (a) passing a liquid or gaseous form of the mixture of compounds over or through a bed or column containing the stationary phase of the first form of the invention; and
- (b) detecting or recovering the separated compounds that exit the bed or column.

The chromatography column is preferably a packed column and the packing material is a particulate solid of relatively uniform size with a specific mesh size.

The reaction between the phenol-derivatives and the aldehydes may be catalysed by acid or base. Under these conditions, polymeric condensation products are formed. Most preferably, a base such as sodium carbonate catalyses the reaction.

Whilst it is contemplated that any phenol-derivative may be suitable for the preparation of the stationary phase, in a preferred form of the invention the phenol-derivative is resorcinol. Similarly, a number of aldehydes and base catalysts can be used in the reaction to form the coating material. However, in a preferred form of the invention, the aldehyde is formaldehyde (or a source thereof) and the base catalyst is sodium carbonate.

In a further preferred form of the invention, the stationary phase may be formed by reacting resorcinol with paraformaldehyde in an aqueous solution containing a 1:1 to 2:1 (w/w) ratio of paraformaldehyde to resorcinol, and a 10:1 to 20:1 (w/w) ratio of resorcinol to sodium carbonate. The reaction may be carried out at about 60°C to about 80°C. Upon completion of the reaction, the pH of the reaction mixture is preferably adjusted to 6 to 7 and excess aqueous solvent is separated from the reaction mixture. The solvent may be removed by distillation at reduced pressure for example.

The reaction product is then preferably added in dropwise fashion to the particulate support material with heating to about 150°C to about 200°C with mixing. The amount of reaction product that is added to the support material may be 1%, 2%, 5% or 10% (w/w).

The particulate support material may be any suitable material that is used for that purpose in the art, including silica and alumina. Most preferably however, the particulate support material is silica.

Silica is available in a wide range of particle sizes. As is known in the art, the size of the stationary phase particles in packed columns can have an effect on the performance of the stationary phase. For the purposes of the present invention, the silica support material preferably has a particle size of about 100 to about 300 microns, and more preferably about 125 to about 212 microns.

Columns containing the stationary phase of the present invention may be used to separate any suitable mixture of compounds. However, the inventor has

found that the stationary phase is particularly suited to the separation of mixtures of hydrocarbons, and in particular to separations of petrochemical mixtures such as liquefied natural gas.

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#### Brief Description of the Figures

The invention will now be illustrated with reference to the accompanying figures in which :-

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Figure 1 shows an elution profile for the analysis of a gas phase sample of LNG on an AMPAK 1-1 column; and

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Figure 2 shows an elution profile for the analysis of a liquid phase sample of LNG on an AMPAK 1-1 column.

#### Detailed Description of the Invention

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As mentioned previously, the resinous coating material that is prepared according to the methods described herein can be used in a packed column. For the purposes of further description and discussion of the invention, reference will be made to a packed column using a particulate solid support material with which the resinous coating material is reacted. However, it will be appreciated that the invention is not to be restricted to that specific embodiment.

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In preparing the stationary phase, the resinous coating material is formed initially. The resinous coating material ultimately reacts with the stationary phase. To form the resinous material, an aldehyde is reacted with a phenol-derivative under base catalysed conditions.

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The aldehyde component of the resinous coating material can be any suitable aldehyde, including formaldehyde, acetaldehyde, glyoxal, furaldehyde, benzaldehyde, hydroxybenzaldehyde or chloroacetaldehyde. Most preferably, the aldehyde is formaldehyde or any formaldehyde derivative that is known in

the art to be useful in conjunction with phenol-formaldehyde resins. A source of formaldehyde is preferably used as the aldehyde component. For example, a formalin solution containing either 37 or 50 weight percent formaldehyde in water may be used as a source of formaldehyde. Alternatively  
5 hexamethylenetetramine may be used as a formaldehyde equivalent. Most preferably, however, the formaldehyde source is paraformaldehyde in the form of paraformaldehyde powder that, in solution, provides an equilibrium concentration of formaldehyde. The aldehyde component may also be a mixture of two or more aldehydes.

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The phenol component of the resinous coating material may be phenol itself (i.e., hydroxybenzene) or any other suitable phenol derivative, including substituted phenols such as cresols and xylenols, or a di- or polyhydric phenol. Examples of di- or polyhydric phenols that may be suitable for this purpose  
15 include: resorcinol, o-cresol, p-cresol, p-tertbutylphenol, p-nonylphenol, p-dodecylphenol, difunctional xylenols, catechol, dihydroxybiphenol, trihydroxybiphenol, hydroquinone, alkylidenebisphenols or thio-bisphenols. The phenol component may also be a mixture of two or more these compounds. Most preferably, the phenol component is resorcinol.

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The resinous coating material may be obtained by heating the phenol and the aldehyde in the presence of a base catalyst. Useful base catalysts include those known in the art, for example, sodium carbonate, potassium carbonate, sodium hydroxide or potassium hydroxide. Most preferably the base catalyst is  
25 sodium carbonate. The catalyst may also be a mixture of two or more base catalysts.

Although the levels of base catalyst may be adjusted, the base is preferably added to the reaction mixture at a resorcinol:sodium carbonate ratio of about  
30 10:1 to about 20:1 (w/w). This amount of base catalyst is thought to provide a material having desirable properties of the coating material, whilst allowing for sufficiently rapid cure.

Specifically, a resinous coating material in accordance with the present invention is produced by mixing 90 parts by weight of the phenol compound, 105 parts by weight of the aldehyde compound and 5 parts by weight of sodium carbonate in water, and conducting the reaction at a reaction temperature of 60-90°C for at least 2 hours. In the case of the reaction of resorcinol with formaldehyde, the reaction is preferably maintained at a reaction temperature of about 70°C for about 2 hours. Although the relative amounts of resorcinol and formaldehyde have been separately described, it is contemplated that pre-reacted resins of resorcinol and formaldehyde could also be used.

Normally, the resorcinol-formaldehyde condensation product is formed first and then it is added to the silica. However, this is only a preferred procedure and the reactants (the resorcinol and formaldehyde) can be added to the silica in an uncondensed form and the entire condensation can then take place *in situ*.

It is believed that the resinous coating material is produced in a methylation reaction between the phenol and the aldehyde in the presence of the base catalyst. Optionally, the phenol-aldehyde condensation product may be further modified with a modifier. For example, a second phenol or derivative may be used to modify one or more properties of the product, such as the polarity or the viscosity.

Following the condensation reaction between the phenol and the aldehyde, the reactor is preferably heated to an elevated temperature (preferably in the range of about 60°C to about 90°C, and most preferably at about 70°C) and held at this temperature until a product of desired viscosity is produced. The temperature of the reaction is preferably controlled in order to prevent overheating.

The reaction is carried out using water as the solvent. However, any other suitable solvent may be used. Upon completion of the reaction, the solvent may be removed using any suitable solvent removal technique, such as distillation.

The solid support material may be any material that is used for that purpose in the art. For example, alumina and silica are common support materials. Most preferably, the support material is silica. In particular, commercially available silica gel having particle size of 125 to 212 $\mu$ m is found to be suitable.

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Prior to reacting the silica with the resinous coating material, it is preferably preactivated by treating the silica with a catalytic amount of a activating substance that activates the silica and promotes adsorption and/or bonding of the resinous coating material to the silica particles. Many activating substances for this purpose are known in the art, and for example acetic anhydride is found to be suitable for the purposes of the present invention. Thus, the silica is preferably stirred and heated to about 80°C in the presence of acetic anhydride for about 15 minutes. Preferably about 0.1 to 1% (w/w) acetic anhydride is used, and most preferably about 0.5 % (w/w) acetic anhydride is used.

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Following activation of the silica, the resinous coating material is added dropwise with heating. The amount of resinous coating material to be added will depend on the density of liquid phase required on the support material. In preferred embodiments, 1, 2, 5 or 10% (w/w) of resinous coating material is added. The silica mixture is preferably heated at between 150°C and 200°C until the reaction has abated as evidenced by a slowing or ceasing of the evolution of fumes and moisture from the mixture.

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The stationary phase so obtained is then suitable for packing into columns using standard techniques. The column may be a metal (stainless steel or copper) or glass tube of various lengths.

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The gas chromatography columns of the present invention can be used in any suitable gas chromatograph. Briefly, during use of the columns an inert carrier gas passes through the column and transports the solute from an injection port to a detector. Hydrogen, helium, and nitrogen are the most common carrier gases. The movement of the mixture of compounds along the column will depend on their volatilities - the more volatile a component, the more time spent in the gas phase and the faster it will be swept along. The various components

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of a mixture will also have different affinities for the stationary phase over which the mobile gas phase flows. Thus, for two components having the same volatilities but differing structures and polarities, their rates of passage will be different.

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Because volatility is an important factor in gas chromatography, the column is generally contained in an oven, the temperature of which can be closely and reproducibly controlled. For very volatile compounds, the oven may be operated at only 30 to 40 °C but, for relatively involatile substances, 10 temperatures of 200 to 250 °C may be needed. For GC analysis, the column may be operated at one fixed temperature (isothermally) or over a temperature range (temperature programming).

15 In general, the longer a chromatographic column, the better will be separation of mixture components.

The sample to be analysed is commonly injected from a syringe by insertion through a rubber septum in an injector, and the entire sample is vaporised immediately and swept directly into the column.

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A detector monitors the carrier gas stream as it passes out of the column. The signal produced by a compound eluting from the column is generally proportional to the concentration or the total amount of compound present. Thermal conductivity detectors (TCD) and the flame ionisation detectors (FID) 25 are two common types of detectors.

#### Description of Preferred Embodiments of the Invention

30 The invention will now be further described with reference to specific embodiments of the invention. It will be appreciated that the invention is not to be limited to these particular embodiments.

The inventor's research on the preparation of new chromatographic stationary phases for gas chromatographic applications have lead to the formulation of

new stationary phases of the present invention, which are called 'AMPAK' columns herein.

5 The performance of these packed columns (1.5m x 0.5cm ID & 1.5m x 0.75cm ID) have been tested using a SHIMADZU GC-TCD system. Several petroleum hydrocarbon standards (gas and liquid phase), aliphatic and aromatic hydrocarbons mixtures, (C<sub>1</sub>-C<sub>34</sub>) were analysed and tested, along with selected petroleum products (LPG, LNG, GPP – C<sub>3</sub>, GPP – i-C<sub>4</sub> & n-C<sub>4</sub> and hydrocarbons type of refrigerant). The analysis results have shown that the  
10 new AMPAK series packed columns could perform successfully on the above mentioned hydrocarbon standards and samples. Especially notable is the separation of the butane isomers (i-C<sub>4</sub> & n-C<sub>4</sub>) with high resolution ( $\Delta t_r$ ) between peaks of the isomers. This high resolution of the isomeric components on AMPAK series packed columns had shown to be much higher than the  
15 literature data available for commercially available HaySep™, Chromosorb™ and Porapak™ columns.

Molecular sieve 5A & 13X, silica gel and OV-1 (1%) stationary phases were also tested at the same conditions as the AMPAK packed columns. The results  
20 obtained were compatible with the literature data. However, some of these tested packing materials showed no sign of separating the butane isomers, whilst some of them showed a little separation of the butane isomers, when compared to the AMPAK columns and under the same column conditions.

25 Studies on the stability, durability and aging of the AMPAK packed columns have shown that they are stable during the analysis by GC-TCD system. During investigations on the performance of the AMPAK packed columns and retention time correlations with the commercially available GC data for the analysis of the liquid LNG sample and other related petroleum products, it was  
30 found that AMPAK columns are capable of performing analyses in a single run (C<sub>1</sub>-C<sub>34</sub> aliphatic and aromatic mixtures) on one column. Of course, it is also possible to link one AMPAK column to another non-AMPAK packed column with 1 or 2 switching valves and an additional FID detector (besides the TCD detector) to detect the low concentrations of C<sub>5</sub>-C<sub>34</sub> components. In the

petroleum industry, analysis of LNG and other petroleum related products usually takes place by using 5 or 9 columns with multi switching valves.

#### *Example 1 – Gas Chromatography Procedure*

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Gas chromatography was carried out using a Shimadzu Gas Chromatograph, model 8A 2.

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The column oven was fitted with one stainless steel column that was used as a reference column and one glass column that had a 1.5m length and 0.5cm internal diameter and that was packed with a specific stationary phase.

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Gas flow measurements were conducted using a soap-film flowmeter consisting of a calibrated 10ml burette with glass rubber teat on the bottom containing liquid soap. The gas was bubbled through the soap, and after the walls were thoroughly wetted the time for given bubble to travel through the burette was measured by stopwatch. Constant flow rates of carrier gas, helium (10ml/23s), to both columns were maintained by means of a single precision pressure regulator and two precision mass flow regulators.

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For any programmed temperature chromatography the column oven temperature was manually carried out.

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The sample injection port was maintained at 200°C, which is higher than the boiling point of sample components ( $C_1$ - $C_{11}$ ) and for sample components ( $>C_{11}$ ). Theoretically, the microgram amount present will eventually turn these components to gas phase.

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A Thermal Conductivity Detector (TCD) was used to detect separated compounds. In a TCD, thermistors are used as sensing elements to determine the change in thermal conduction of the sample stream as opposed to a reference stream of pure carrier gas. A differential signal is obtained by the change in heat loss from the element due to the presence of a sample

component in the column effluent. The intensity of the signal is proportional to the concentration of sample in the detector at the time.

The response of the TCD was logged through a SHIMADZU C-R6A  
5 CHROMATOPAC programmable integrator/recorder to optimise the results obtained.

10 The standards, chemical solvents and solutions used were as follows:

1. Specially mixed Hydrocarbons Standard Gases ( $C_1$ - $C_4$ ):
  - i. mixtures I –  $CH_4$  (balance),  $C_2H_6$  (20%),  $C_3H_8$  (25%),  $n-C_4H_{10}$  (25%)] &
  - ii. mixtures II –  $CH_4$  (balance),  $C_2H_6$  (20%),  $C_3H_8$ (20%),  $i-C_4H_{10}$  (20%),  $n-$   
15  $C_4H_{10}$ (20%)
2. n-Pentane, supplied by BDH Laboratory Supplies, England.
3. n-Hexane, supplied by BDH Laboratory Supplies, England.
4. n-Heptane (fractions), supplied by BDH Laboratory Supplies, England.
5. i-Octane, supplied by Merck, Germany.
- 20 6. Benzene, supplied by Fluka, USA.
7. Toluene, supplied by J.T.Baker, USA.
8. Xylenes, supplied by Merck, Germany.
9. Mixture of  $n-C_{12}$ ,  $n-C_{14}$ ,  $n-C_{16}$ ,  $n-C_{18}$ ,  $n-C_{20}$ ,  $n-C_{22}$ ,  $n-C_{24}$ ,  $n-C_{26}$ ,  $n-C_{28}$ ,  $n-C_{32}$ ,  
 $n- C_{34}$ ,  $n-C_{36}$ , dissolved in n-Hexane.
- 25 10. Mixture of  $n-C_{28}$ ,  $n-C_{29}$ ,  $n-C_{30}$ ,  $n-C_{32}$  dissolved in n-Hexane.
11. Resorcinol.
12. Paraformaldehyde powder.
13. Sodium bicarbonate.
14. Acetic anhydride.

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The stationary phases used were as follows:

15. Packing Materials –
  - i. Molecular Sieves 13X (size 355-500 $\mu$ m, ALDRICH SIGMA)

- ii. Molecular Sieves 5A (size 355-500 $\mu$ m, ALDRICH SIGMA)
  - iii. OV-1 (1%)
  - iv. Silica Gel (125-212 $\mu$ m, FLUKA Silica gel 60)
  - v. Modified Packing Materials (AMPAK series)
- 5 16. Helium (Malaysian Oxygen Bhd.)

The petroleum product samples used were as follows:

- 17. Hydrocarbon type of refrigerant sample.
- 10 18. Liquefied Petroleum Gas (LPG) sample.
- 19. Liquefied Natural Gas (LNG) sample.
- 20. Natural Gas sample.
- 21. Gas Petroleum Products (GPP, C<sub>3</sub>) sample
- 22. Gas Petroleum Products (GPP, i-C<sub>4</sub> & n-C<sub>4</sub>) sample.

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#### *Example 2 – Preparation of molecular sieve stationary phases*

Commercially available molecular sieve zeolites (molecular sieve 13X and molecular sieve 5A, Sigma Aldrich) were pellet shaped when purchased and in order to obtain the desired particle size, the sieves were ground to smaller particle sizes using a grinding machine (SAINTIFIK MAJU). The ground stationary phases (particles) were then sieved through a combination of sieving trays (mesh trays) with the help of "jolting machine".

#### *Example 3 – Preparation of AMPAK stationary phases*

##### *3.1 – Preparation of the resinous coating material*

A 1-litre 3-necked round bottom flask was equipped with a reflux condenser, stirrer and thermometer. To this flask was added resorcinol (90g), paraformaldehyde powder (105g), sodium carbonate (5g) and distilled water (200ml). The reaction mixture was stirred and heated in an oil bath at 70°C for 2hrs. Two layers formed if stirring was stopped. Sufficient 10% sulfuric acid was added to reduce the pH to 6-7. Vacuum was then applied by means of a water aspirator (pressure regulated at about 30-50mmHg) and the water was

removed through the condenser, which was modified for distillation. The temperature of the reaction mixture was not allowed to exceed 70°C. Samples were withdrawn every 15min and tested for gel time and TLC analysis. The final dark-brownish viscous resinous product was then further tested by HPLC and GC.

### 3.2 – Preparation of the stationary phase

In a 250ml beaker, the silica gel support material (20g, 125-212µm) was first treated with acetic anhydride (0.5%, w/w) and heated at 80°C on a hot plate with continuous mixing for 15min. Then the viscous resinous product from above (as in 3.1) was added (1;2;5 or 10%, w/w) in a dropwise manner with continuous heating (150-200°C) and mixing with a glass rod for 1hr. This process was continued until the evolution of fumes and moisture had abated and the colour of the material had changed from white to dark-brown solid product.

#### *Example 4 – Use of AMPAK stationary phases*

The AMPAK product from 3.2 was packed into a glass or stainless steel column. Glass type columns of 1.5m (length) x 0.5cm (Internal Diameter, ID) and 1.5m (length) x 0.75cm ID were constructed by a glass blower. Alternatively, a commercial glass type column of 2m (length) x 0.5cm OD was used.

The column was packed according to the following procedure:

- Care was exercised when packing the glass columns to obtain uniform packing density throughout. Vibrating, tapping, banging, tamping, and slurry packing procedures were used.
- The empty column was weighed ( $\pm 0.1$ g) before packing any stationary phases into the columns.
- In packing the column, even packing is desirable so that the gas flow does not vary considerably throughout the column (too much void volume). A funnel was attached to one open end of the column by rubber tubing; the other end was plugged with glass wool and vacuum

was applied at this end. The particulate stationary phase was then poured into the funnel and the column was vibrated, tapped, or tamped to obtain a evenly packed column.

- 5 The newly packed columns were conditioned firstly with helium carrier gas. The activation was accomplished for molecular sieve columns at 250°C for 10 hours and for the modified silica gel (AMPAK) at 200°C for 6 hours. Then a gentle flow of helium was passed through the column with heating at temperature programming 23-280°C (1°C/min).

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#### *Example 5 - Gas Sample Injection Method*

- Gas tight syringes were used (25µl and 5ml, provide by VICI Precision  
15 Sampling, Inc) for all gas sampling procedures. Various volumes of atmospheric air were injected (as the standard and calibration gas) into the injection port before injecting any of the samples, and this step was repeated at least three times for reproducible results.

- 20 A sample of about 1.0µl or any other selected volume of the Hydrocarbons [C<sub>1</sub>–C<sub>4</sub>] Standard Gases Mixtures either I or II were injected immediately into the column, after being carefully taken from a gas tight sample loop port, that is to be connected in two ways. One is connected to the standard gases mixture and was fitted with a pressure gauge, and the other was connected to the  
25 commercial sample cylinder which was fitted with a metal filter. Finally, both of these gas inlets were connected to a three-way valve sample collection outlet. That is from this loop the gas was taken for injection to the GC-TCD via a gas tight syringe.

- 30 However, it is preferred to flush the syringe with the samples gas before injecting any of this gas samples to the GC.

For any injection of hydrocarbons (C<sub>1</sub>–C<sub>7</sub>) mixtures, a 25µl luer-lock gas tight syringe was used to withdraw 1µl liquid mixture of n-C<sub>5</sub>, n-C<sub>6</sub> & n-C<sub>7</sub> (v/v) ratio

(1:1:1) before collecting the Standard Gases Mixture II (C<sub>1</sub>–C<sub>4</sub>) from the sample collection loop.

*Example 6 - Liquid Phase Sampling Procedures*

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2-5µl of n-hexane solvent was injected before any injection of hydrocarbon (C<sub>12</sub>–C<sub>36</sub>) mixtures. This was to mark the retention time of n-hexane at the chosen operating conditions.

10 Each of the eluted components from the different chromatograms was marked, by:-

- Injecting a mixture of n-C<sub>12</sub>, n-C<sub>14</sub>, n-C<sub>16</sub>, n-C<sub>18</sub>, n-C<sub>20</sub>, n-C<sub>22</sub>, n-C<sub>24</sub>, n-C<sub>26</sub>, n-C<sub>28</sub>, n-C<sub>32</sub>, n-C<sub>34</sub>, n-C<sub>36</sub> dissolved in n-Hexane; or injecting

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acolumn conditions.

CLAIMS

1. A vapour-producing product for disinfecting a space comprising one or more essential oils or essential oil components, and a mixture of volatile and non-volatile solvents absorbed on a solid carrier, wherein the percentage weight ratio of volatile to non-volatile solvent is 3:1 to 1:3.
2. A product according to claim 1, wherein the essential oil component is cinnamic aldehyde.
3. A product according to claim 1, wherein the essential oil component is cinnamic alcohol.
4. A product according to claim 1, wherein the essential oil component is eugenol.
5. A product according to any preceding claim, wherein the essential oil is tea tree oil.
6. A product according to any claims 1 to 4, wherein the essential oil is cinnamon oil.
7. A product according to any preceding claim, wherein the volatile solvent is an alcohol.
8. A product according to claim 7, wherein the alcohol is iso-propanol.
9. A product according to any preceding claim, wherein the non-volatile solvent is water.
10. A product according to any claims 1-8, where in the non-volatile solvent is a glycol.
11. A product according to claim 10, wherein the glycol is monopropylene glycol.
12. A product according to any preceding claim, wherein carrier is a resilient or rigid material, is amorphous silicon dioxide or is a non-woven material comprising cellulosic fibres and plastic.
13. A product according to claim 12, wherein the non-woven carrier is a combination of cellulose and polypropylene.
14. A product according to any of claims 1 to 11, wherein the carrier is cardboard.
15. A product according to any of claims 1 to 11, wherein the carrier is sintered plastic.

16. A product according to any of claims 1 to 11, wherein the carrier is amorphous silicon dioxide.
17. A product according to claim 14, wherein the cardboard carrier has one dimension of at least 200mm.
- 5 18. A product according to any claims 1 to 11, wherein the carrier is a self adhesive item or label.
19. A vapour-producing formulation comprising one or more essential oils or essential oil components as defined in any preceding claim, and a mixture of volatile and non-volatile solvents as defined in any preceding claim is a
- 10 viscous liquid, wherein the ratio of volatile to non-volatile solvent is 3:1 to 1: 3.
20. A formulation according to claim 19, wherein the viscosity is modified by addition of silicon dioxide.
21. Use of a product or formulation according to any preceding claim, to sanitise and deodorise a waste disposal bin.
- 15 22. A waste disposal bin comprising a product or formulation according to any of claims 1 to 20.